

# SOIL SCIENCE

VOLUME 40  
JUNE-DECEMBER, 1935

RUTGERS UNIVERSITY  
NEW BRUNSWICK, NEW JERSEY  
U. S. A.

PUBLISHED BY  
THE WILLIAMS & WILKINS COMPANY  
BALTIMORE, MARYLAND

# SOIL SCIENCE

Editor-in-Chief  
JACOB G. LIPMAN

Associate Editor  
HERMINIE BROEDEL KITCHEN

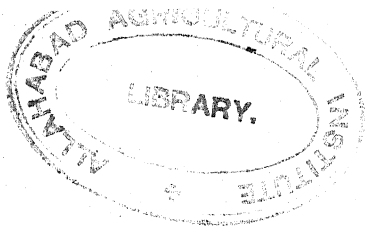
## ADVISORY STAFF

A. W. BLAIR, J. S. JOFFE, L. L. LEE, H. C. McLEAN, G. T. NIGHTINGALE, A. L. PRINCE, J. W. SHIVE, H. B. SPRAGUE, R. L. STARKEY, AND S. A. WAKSMAN, New Jersey Agricultural Experiment Station, New Brunswick, N. J.

## CONSULTING EDITORS

- F. J. ALWAY  
University of Minnesota, St. Paul,  
Minn.
- K. ASO  
Imperial University, Tokyo, Japan
- C. BARTHEL  
Lantbrukshögskolan, Uppsala, Sweden
- RICHARD BRADFIELD  
College of Agriculture, Ohio State  
University, Columbus, Ohio
- P. E. BROWN  
Iowa State College of Agriculture,  
Ames, Iowa
- B. C. BURT  
Imperial Council of Agricultural Re-  
search, New Delhi, India
- H. J. CONN  
New York State Experiment Station,  
Geneva, N. Y.
- ALBERT DEMOLON  
Ministry of Agriculture, Paris, France
- E. B. FRED  
University of Wisconsin, Madison, Wis.
- V. V. GEMMERLING  
Agricultural Experiment Station, Gem-  
bloux, Belgium
- B. L. HARTWELL  
143 Armington St., Edgewood, R. I.
- D. J. HISSINK  
Soil Science Institute, Groningen, Hol-  
land
- O. LEMMERMANN  
Institut für Agrikulturchemie u. Bak-  
teriologie der Landwirtschaftlichen  
Hochschule, Berlin-Dahlem, Ger-  
many
- C. B. LIPMAN  
University of California, Berkeley,  
Calif.
- BURTON E. LIVINGSTON  
Johns Hopkins University, Baltimore,  
Md.
- HENRIK LUNDEGÅRDH  
Centralanstalten för jordbruksförsök,  
Stockholm, Sweden
- T. L. LYON  
Cornell University, Ithaca, N. Y.
- M. M. MCCOOL  
Boyce-Thompson Institute, Yonkers,  
N. Y.
- W. H. MACINTIRE  
University of Tennessee, Knoxville,  
Tenn.
- S. MATTSON  
Lantbrukshögskolan, Uppsala, Sweden
- E. A. MITSCHERLICH  
University of Königsberg, Prussia
- C. A. MOOERS  
University of Tennessee, Knoxville,  
Tenn.
- D. N. PRIANISHNIKOV  
Timiryazev Academy, Moscow, U. S.  
S. R.
- THEO. REMY  
Institut für Boden- und Pflanzen-  
baulehre, Bonn a. Rh., Prussia
- G. ROSSI  
Royal Agricultural High School in  
Portici, Naples, Italy
- E. J. RUSSELL  
Rothamsted Experimental Station,  
Harpenden, England
- O. SCHREINER  
U. S. Department of Agriculture,  
Washington, D. C.
- ALEXIUS A. J. DE'SIGMOND  
Royal Hungarian Joseph University of  
Technical Sciences, Budapest, Hun-  
gary
- J. STOKLASA  
Technical High School, Prague, Czecho-  
slovakia
- CHAS. E. THORNE  
Ohio Experiment Station, Wooster,  
Ohio
- N. M. TULAIOV  
Agricultural Experiment Station, Sar-  
atov, U. S. S. R.
- G. WIEGNER  
Landwirtschaftliche Hochschule, Zür-  
ich, Switzerland
- S. WINOGRADSKY  
Pasteur Institute, Paris, France





## CONTENTS

Jacob Goodale Lipman—Biographical Sketch.....	1
Jacob G. Lipman and Soil Science. E. J. RUSSELL.....	3
Jacob G. Lipman as an Investigator. SELMAN A. WAKSMAN.....	11
Jacob G. Lipman and New Jersey Agriculture. A. W. BLAIR.....	25
Jacob G. Lipman as Teacher and Director of Research. ROBERT V. ALLISON.....	31
Early Fertilizer Work in the United States. OSWALD SCHREINER.....	39
The Beginnings and Development of Soil Microbiology in the United States. P. E. BROWN.....	49
The Method in Soil Microbiology as Illustrated by Studies on Azotobacter and the Nitrifying Organisms. S. WINOGRADSKY.....	59
Development of Soil Science. ALEXIUS A. J. DE'SIGMOND.....	77
The Influence of the Soil Upon the Growth of the Plant. HENRIK LUNDEGÅRDH.....	89
The Agronomic Importance of Calcium. W. P. KELLEY.....	103
The Clay Content of the Soil as Related to Climatic Factors, Particularly Temperature. HANS JENNY.....	111
Sorption of Phosphates by Non-Calcareous Hawaiian Soils. L. E. DAVIS.....	129
A New Method of Estimating Exchangeable Bases in Soils. AMAR NATH PURI.....	159
A Comparison Between the Suction Method and the Centrifuge Method for Determining the Moisture Equivalent of Soils. GEORGE JOHN BOUYOUCOS.....	165
A Machine for the Subsurface Treatment of Soils with Chloropicrin and with Carbon Bissulfide for Nematode Control Under Field Conditions. J. R. NELLER AND R. V. ALLISON.....	173
A Comparative Study of the Bacterial Flora of Windblown Soil: VI. Death Valley, California, with Summary of Six Soil Studies. LAETITIA M. SNOW.....	181
Phosphate Fixation in Soils, Particularly as Influenced by Organic Matter. J. L. DOUGHTY.....	191
Fluorine, Its Effect on Plant Growth and Its Relation to the Availability to Plants of Phosphorus in Phosphate Rocks. R. P. BARTHOLOMEW.....	203
The Effect of Nitrogen Content of Rye on its Rate of Decomposition. W. B. ANDREWS.....	219
Some Chemical and Biological Changes Produced in a Fox Sandy Loam by Certain Soil Management Practices. L. S. CARTER.....	223
Absorbed Sodium in Soils as Affected by the Soil-Water Ratio. FRANK M. EATON AND V. P. SOKOLOFF.....	237
Estimation of Replaceable Na and K, Exchange Capacity, and Degree of Alkalization in Alkali Soils by Ammonium Carbonate Extraction. AMAR NATH PURI.....	249
The Laws of Soil Colloidal Behavior: XVII. Magnesium Silicate—Its Base-Exchange Properties. J. S. JOFFE, L. T. KARDOS AND SANTE MATTSON.....	255
Mathematical Relations Between Total Exchange Capacity and Absorption of Ammonium and Potassium by Soils. J. F. FUDGE.....	269
Soil Temperature Apparatus for Field Work. G. ALLEN MAIL.....	285
Corrosiveness of Certain Ohio Soils. I. A. DENISON AND S. P. EWING.....	287
A Comparison of Potassium Permanganate and Ceric Sulfate for the Oxidation of Cobaltinitrite in the Estimation of Potassium in KCl Solution and in Ammonium Acetate Soil-Extracts. HENRY C. HARRIS.....	301
Organic Soil Carbon by Reduction of Chromic Acid. L. E. ALLISON.....	311

The Chemical and Biological Nature of Certain Forest Soils. W. L. POWERS and W. B. BOLLEN.....	321
Microbial Activities in Soil: II. Activity of Specific Groups of Microbes in Relation to Organic Matter Transformation in Palouse Silt Loam. S. C. VANDECAVEYE AND M. C. ALLEN.....	331
Curtis F. Marbut, 1863-1935.....	345
Chemical Nature of Organic Matter in Different Soil Types. SELMAN A. WAKSMAN AND I. J. HUTCHINGS.....	347
The Availability of Soil Potassium. JOHN LAMB, JR.....	365
A Simple Method of Estimating Exchangeable Calcium and Other Bases in Non-Calcareous Soils. AMAR NATH PURI.....	383
A Device for Measuring Precipitation Waters Lost from the Soil as Surface Runoff, Percolation, Evaporation, and Transpiration. G. W. MUSGRAVE.....	391
Sorption of Liquids by Soil Colloids: II. Surface Behavior in the Hydration of Clays. L. D. BAVER AND HANS WINTERKORN.....	403
John Sharkey Carroll, 1871-1935.....	421
The Relation of Soil Treatment to the Nodulation of Peanuts. H. B. MANN.....	423
The Relation of Soil Erosion to Certain Inherent Soil Properties. J. F. LUTZ.....	439
The Influence of Exchangeable Sodium in the Soil on its Properties as a Medium for Plant Growth. E. I. RATNER.....	459
A Sedimentation Tube for Analyzing Water-Stable Soil Aggregates. R. C. COLE AND N. E. EDLEFSEN.....	473
A Method for Making Mechanical Analysis of the Ultimate Natural Structure of Soils. GEORGE JOHN BOUYOUCOS.....	481
The Role of Plant Constituents in the Preservation of Nitrogen in the Soil. SELMAN A. WAKSMAN AND I. J. HUTCHINGS.....	487

# ILLUSTRATIONS

## PLATES

### SPECIAL ISSUE DEDICATED TO DOCTOR LIPMAN

Jacob Goodale Lipman.....	<i>Frontispiece</i>
Plate 1. The Campus of the New Jersey Agricultural Experiment Station.....	9
Plate 2. Members of the Department of Soil Chemistry and Bacteriology of the New Jersey Agricultural Experiment Station, 1932.....	37
Plate 3. Doctor Lipman and Two Prominent Visitors to the Experiment Station in 1927.....	87

### A COMPARISON BETWEEN THE SUCTION METHOD AND THE CENTRIFUGE METHOD FOR DETERMINING THE MOISTURE EQUIVALENT OF SOILS

Plate 1. The Suction Method for Determining Moisture Equivalent in Soils.....	171
---	-----

### A MACHINE FOR THE SUBSURFACE TREATMENT OF SOILS WITH CHLOROPICRIN AND WITH CARBON BISULFIDE FOR NEMATODE CONTROL UNDER FIELD CONDITIONS

Plate 1. Fig. 1. General view of the experimental machine showing the liquid supply tank and hose connection with the pipe leading to the subsurface outlet.....	179
2. Detail of the dispensing system.....	179

### THE CHEMICAL AND BIOLOGICAL NATURE OF CERTAIN FOREST SOILS

Plate 1. Growth of Oats in Sand Cultures Kept Moist with Culture Solution Lacking Nitrogen, and Supplied with 1.5 Gm. Nitrogen in Forest Soil Layers.....	329
---	-----

Curtis F. Marbut.....	<i>Frontispiece</i>
-----------------------	---------------------

### A DEVICE FOR MEASURING PRECIPITATION WATERS LOST FROM THE SOIL AS SURFACE RUNOFF, PERCOLATION, EVAPORATION, AND TRANSPIRATION

Plate 1. Fig. 1. Method of sinking cylinder into selected soil area.....	397
2. Two cylinders sunk to full depth, one of which has hooks attached ready for fastening to hoist.....	397
3. Gravel pan in position upon base.....	397
Plate 2. Fig. 1. The cylinder in position upon the gravel pan and the operation of sealing a joint between the pan and cylinder with a preparation of silica, asphalt, and asbestos.....	399
2. Reinforcement in position for constructing concrete shoulder about base of cylinder and including pan. Also a view of one such base complete.....	399
3. Four cylinders in position, with the completed base.....	399
Plate 3. Fig. 1. Undisturbed condition of soil in cylinder after being sunk to its full depth. The original vegetation and the original soil slope remain..	401
2. Cylinders spaced equi-distant from one another and from central cellar.	401

### THE RELATION OF SOIL TREATMENT TO THE NODULATION OF PEANUTS

Plate 1. Excessive Nodulation on the Roots of Inferior Peanuts Grown on Portsmouth Fine Sandy Loam (pH 5.5).....	433
--	-----

Plate 2. Nodulation of Peanuts in Virgin Norfolk Sandy Loam (pH 5.0) as Affected by Applications of Calcium Carbonate.....	435
Fig. 1. Nodules per pot of five plants 35 days after planting.....	435
2. Nodules per pot of five plants at maturity, 146 days after planting....	435
Plate 3. Nodulation of Peanuts in Virgin Coxville Fine Sandy Loam (pH 4.5) as Affected by Applications of Calcium Carbonate.....	437
Fig. 1. Nodules per pot of five plants 31 days after planting.....	437
2. Nodules per pot of five plants at maturity, 115 days after planting....	437

#### THE INFLUENCE OF EXCHANGEABLE SODIUM IN THE SOIL ON ITS PROPERTIES AS A MEDIUM FOR PLANT GROWTH

Plate 1. The Influence of Exchangeable Sodium in Chernozem Soil upon the Growth of Spring Wheat.....	471
--	-----

### TEXT-FIGURES

#### THE INFLUENCE OF THE SOIL UPON THE GROWTH OF THE PLANT

Fig. 1. Diagram of the Antagonistic Action of One Ion ( $M_0$ ) on the Absorption of a Second Ion ( $M_1$ ).....	92
2. The Relation between the Inner Concentration of Potassium in the Leaves of Oats and the Growth.....	93
3. The Relation between the Amount of Available Potassium in the Soil and Its Concentration in the Plant (Oats).....	96
4. The Relation between the Amount of Calcium and Magnesium in the Soil (from Extracts with Citric Acid) and the Concentration of These Elements in the Plant (Oats).....	97
5. The Influence of the Calcium Content in the Soil on the Uptake of Manganese in Sugar Beets.....	99

#### THE CLAY CONTENT OF THE SOIL AS RELATED TO CLIMATIC FACTORS, PARTICULARLY TEMPERATURE

Fig. 1. Map Showing the Location of the Counties or Areas Investigated.....	112
2. General North-South Correlation between Clay Content of Soil and Latitude (Annual Temperature).....	118
3. General North-South Correlation between Clay Content of Soil and Latitude (Annual Temperature).....	118
4. Clay-Temperature Function for the Parent Material Group (a) "Granites".....	122
5. Clay-Temperature Function for the Parent Material Group (b) "Gneisses".....	122
6. Clay-Temperature Function for the Parent Material Group (d) "Basic Rocks".....	122
7. Clay-Temperature Function for the Parent Material Group (g) "Granites, Gneisses and Schists".....	122
8. Idealized Clay-Climate Surface, Showing the Variation of "Climatic Clay" in Soils Derived from Granites and Gneisses as a Function of Moisture and Temperature.....	127

#### SORPTION OF PHOSPHATES BY NON-CALCAREOUS HAWAIIAN SOILS

Fig. 1. Equilibria between Soil and Phosphate Solutions.....	133
2. Equilibria between Soil and Phosphate Solutions.....	134
3. Reversal of Equilibria between Soil and Phosphate Solutions.....	142
4. Equilibria between Soil and Potassium.....	145
5. Sorption of Phosphate from Solutions of Different pH Values.....	149
6. Mol Fractions of Phosphoric Acid and Its Ions at Various pH Values.....	149

SOME CHEMICAL AND BIOLOGICAL CHANGES PRODUCED IN A FOX SANDY LOAM BY CERTAIN  
SOIL MANAGEMENT PRACTICES

- Fig. 1. Numbers of Bacteria and Fungi in Relation to Soil Treatment, Soil Reaction,  
Content of Total Nitrogen, Available Phosphorus, and Ignition Loss. . . . . 229
2. Interrelation between Nitrate Production, Content of Available Phosphorus,  
Total Nitrogen, and Ignition Loss, Bacterial Numbers, Crop Yields in the  
Field and Greenhouse, and Carbon Dioxide Production from Field and Green-  
house Samples in Soils Receiving Different Field Treatments. . . . . 232

THE LAWS OF SOIL COLLOIDAL BEHAVIOR: XVII. MAGNESIUM SILICATE—ITS BASE-  
EXCHANGE PROPERTIES

- Fig. 40. The Linear Relationship between the Exchangeable Ca and the Millimols of  
Mg-Silicate Complex Present. . . . . 263

SOIL TEMPERATURE APPARATUS FOR FIELD WORK

- Fig. 1. Soil Temperature Apparatus. . . . . 285

CORROSIVENESS OF CERTAIN OHIO SOILS

- Fig. 1. Typical Section of Pipe Lines Showing Repairs and Soil Data. . . . . 294
2. Relation between Actual and Calculated Repairs. . . . . 296

MICROBIAL ACTIVITIES IN SOIL: II. ACTIVITY OF SPECIFIC GROUPS OF MICROBES IN RELATION  
TO ORGANIC MATTER TRANSFORMATION IN PALOUSE SILT LOAM

- Fig. 1. CO<sub>2</sub> Production and Microbial Development in Soil to Which Stubble Only Was  
Returned for 9 Consecutive Years. . . . . 335
2. CO<sub>2</sub> Production and Microbial Development in Soil Receiving 2,700 Pounds of  
Straw and 370 Pounds Nitrate of Soda Annually for 9 Years. . . . . 335
3. CO<sub>2</sub> Production and Microbial Development in Soil Receiving 2,700 Pounds of  
Straw and 285 Pounds Sulfate of Ammonia Annually for 9 Years. . . . . 336
4. Trend in Decomposition of Organic Complexes in Soil. . . . . 340

THE AVAILABILITY OF SOIL POTASSIUM

- Fig. 1. Effect of the Addition of 5,000 p.p.m. of Dextrin to a Dutchess Silt Loam on the  
Potassium Extracted by NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, on the NO<sub>3</sub> Content, and on the Re-  
sistance Offered to an Electric Current by a 5.1 Water Extract. . . . . 378

A DEVICE FOR MEASURING PRECIPITATION WATERS LOST FROM THE SOIL AS SURFACE RUNOFF,  
PERCOLATION, EVAPORATION, AND TRANSPIRATION

- Fig. 1. Plan and Elevation of Equipment Used in the Measurement of Surface Runoff  
and Percolation from Soil Columns of Undisturbed Structure. . . . . 393

SORPTION OF LIQUIDS BY SOIL COLLOIDS: II. SURFACE BEHAVIOR IN THE HYDRATION OF CLAYS

- Fig. 1. Colloidal Properties of Putnam Clay as Affected by Varying Amounts of Ex-  
changeable Li and K Ions. . . . . 413

THE RELATION OF SOIL EROSION TO CERTAIN INHERENT SOIL PROPERTIES

- Fig. 1. Size-Frequency Distribution Curve of Iredell Sandy Clay Loam with and without  
Dispersion. . . . . 441
2. Size-Frequency Distribution Curve of Davidson Clay with and without Disper-  
sion. . . . . 442
3. Effect of Different Cations upon the Permeability of Davidson Clay Membranes. 451
4. Effect of Different Cations upon the Permeability of Iredell Clay Membranes. . 452

5. Effect of Different Cations upon the Permeability of Putnam Clay Membranes. 452
6. Permeability of Different H-Clay Membranes..... 453
7. Permeability of Different Ca-Clay Membranes..... 454
8. Permeability of Different Na-Clay Membranes..... 454

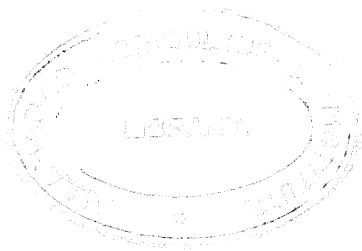
THE INFLUENCE OF EXCHANGEABLE SODIUM IN THE SOIL ON ITS PROPERTIES AS A MEDIUM  
FOR PLANT GROWTH

- Fig. 1. Influence of Increasing Amounts of Exchangeable Sodium upon the Filterability  
of Chernozem Soil..... 463
2. Effect of 3 Years' Application of Various Types of Nitrogen Fertilizers on the  
Filterability of the Soil..... 464
  3. Influence of Exchangeable Na upon the Filterability of Extremely Solonetzic Soil,  
Horizon A..... 464
  4. Influence of Exchangeable Na upon the Filterability of Extremely Solonetzic Soil,  
Horizon B..... 465

A SEDIMENTATION TUBE FOR ANALYZING WATER-STABLE SOIL AGGREGATES

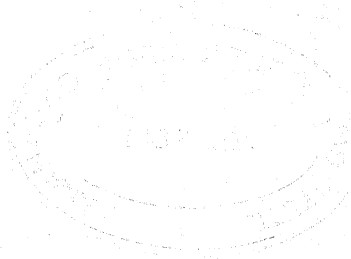
- Fig. 1. Diagram of Sedimentation Tube..... 475
2. Percentage of Particles Having Settling Velocities Equal to or Less than Values  
Indicated on the Graph..... 477





JACOB GOODALE LIPMAN





In his absence on sabbatical leave, 1934-1935,  
the advisory staff of SOIL SCIENCE takes the opportunity  
to dedicate volume 40 of the journal, and especially this number

To

DOCTOR JACOB GOODALE LIPMAN

in honor of his twenty years of editorship  
and his long continued service to soil science and agriculture.



## JACOB GOODALE LIPMAN

### BIOGRAPHICAL SKETCH

Jacob G. Lipman was born in Friedrichstadt, Russia (now Latvia), on November 18, 1874. He received his early education under private tutors in Moscow and later in the gymnasium of Orenburg. In 1888 his family emigrated to the United States and settled very soon afterward on a farm at Woodbine, New Jersey. While assisting his father in caring for the farm, he became interested in the scientific principles underlying agriculture. This led him to become a student of Baron de Hirsch Agricultural School in Woodbine, where he was trained both in practical methods of farming and in certain fundamental principles. The knowledge thus gained did not satisfy him; consequently, upon graduation from the school in 1894, he entered Rutgers College. Here he had an opportunity not only to study the arts and sciences, but, under the inspiring influence of one of his teachers—Professor E. B. Voorhees, an outstanding leader in this country in the field of research in soil and fertilizer chemistry—he decided to devote his future life to this subject. Upon graduation from college in 1898, he went to Cornell University for advanced training in chemistry and in bacteriology; he was at first appointed graduate scholar at that institution, and later, Sage Fellow in Chemistry. He obtained his master of science degree from Cornell in 1900 and his doctor of philosophy degree in 1903. In 1901, he was called back to New Jersey by his former professor to establish a department of soil chemistry and bacteriology at the Agricultural Experiment Station. In 1902 he was appointed instructor in agricultural chemistry at Rutgers College; in 1906 he was made assistant professor; and in 1910, full professor. In 1915, he was made dean of the College of Agriculture. Four years previously, upon the death of Professor Voorhees, he became director of the Experiment Station.

Doctor Lipman has lectured at a number of universities and other institutions in this country and abroad. He is a member of numerous scientific societies and an honorary member of several foreign academies. He holds honorary degrees from different universities and special medals from various scientific societies. He has served on a number of important committees, such as the National Committee on Soil Erosion and various committees of the National Research Council and of the American Society of Agronomy. On several occasions he has acted as special representative of the United States at the International Institute of Agriculture in Rome. He took an active part in the organization of the International Society of Soil Science. At the Prague Conference, he was elected joint-president of the Third Commission on Soil Biochemistry and Bacteriology, and participated actively in the preparation

of the program of this commission for the next conference, which took place in Rome in 1924. At that conference he was elected president of the newly formed International Society of Soil Science. He organized the First International Congress of Soil Science in 1927, in Washington, D. C., which was followed by a special scientific excursion throughout the United States and Canada. In 1929 he received one-third of the first Nitrogen Research Award, made by the Nitrate of Soda Committee of the American Society of Agronomy. He contributed this award to a special fund for furthering soil science at the New Jersey Agricultural Experiment Station. A number of individuals and societies in the state made similar contributions, and the fund became known as the Cook-Voorhees fund, in honor of the first two directors of the New Jersey Experiment Station, prominent in the field of soil science in their own days. This fund is used for assisting foreign scholars who plan to come to the institution for carrying out special investigations in one of the various phases of soil science.

Before the World War, the scientific workers in the United States depended, for necessary scientific literature, upon foreign journals, largely those published in Germany, France, and Great Britain. One of the direct results of the war was to make the United States independent of Europe in this respect. A large number of journals in almost every branch of science were established. Among these, *SOIL SCIENCE* made its appearance in January, 1916. The first issue of this journal was dedicated to E. W. Hilgard, one of the greatest minds in the field of soil science. The journal was first published by Rutgers College. At the end of the third volume, however, it was taken over by the Williams and Wilkins Company of Baltimore, Maryland, and has been published by them uninterruptedly under the editorship of Doctor Lipman. From the beginning, the pages of the journal have been open to workers in soil science in this country and abroad.

This year of his sabbatical leave from the College and Experiment Station is the first time that Doctor Lipman has relinquished, even temporarily, the duties of active editor of the journal. The Editorial Committee takes this opportunity of commemorating the twentieth year of publication of *SOIL SCIENCE* by dedicating this fortieth volume of the journal to its Editor-in-Chief.

In dedicating this volume to Doctor Lipman, the Editorial Committee can pay no higher tribute to him than that which he himself paid to Doctor Hilgard twenty years ago when he said:

"... while the world of science knew of his work and honored him for it, it was the peculiar privilege of his associates to find inspiration in his kind and helpful nature, in his catholic sympathies, in his clear vision and in his unflinching devotion to truth."

## JACOB G. LIPMAN AND SOIL SCIENCE

E. J. RUSSELL

*Rothamsted Experimental Station, England*

There are two ways in which a man may advance science: by his own personal investigations, and by organizing and otherwise facilitating investigations of others. In the usual course a man begins as an investigator; then he is promoted to take charge of his section or department, when he has to lead his team of assistants and students; finally he is entrusted with the care of an entire institution, when he has to maintain its interests in the face of a sceptical and sometimes hostile world—in any event, a world full of noisy claimants for popular favor. And, since nothing succeeds like success, he must ensure success by keeping the whole program as well balanced as possible and helping all departments in their endeavors for advancement, favoring none, repressing none.

Doctor Lipman followed the usual sequence and he has been eminently successful in all the parts he has been called upon to play. There are some who rank as administrators among men of science, and as scientists among administrators. Doctor Lipman, however, is recognized by administrators as a particularly shrewd and able administrator and by scientific workers as a pioneer investigator in soil microbiology. Under his guidance the New Jersey station has always maintained a good level of scientific and practical achievement. It has had no intellectual misfortunes, no "discovery" that had afterwards to be withdrawn because the experimental work was badly done or the deductions loosely drawn; its history has been a continuous record of steady progress in science and service to the community. His ability as an administrator has enabled him to dispense with the adventitious aids of advertisement: in consequence, one finds always at the station a peaceful atmosphere conducive to scientific thought and quiet reflection, perhaps the most important factor in promoting research. "Das dauernde Nachdenken und Durchdenken jeder einzelnen Erscheinung in dem Ackerbau führt immer zu etwas," wrote Liebig to Wöhler in 1862—prolonged meditation and pondering about any agricultural phenomenon is bound to lead somewhere—and the wide open space of the campus, adorned with water and with trees slowly growing into a haunt of ancient peace, shows how Doctor Lipman has striven to satisfy this need for quiet thinking, for the unceasing, unrelenting endeavor toward higher fields of scientific thought and activity.

He began his work at a critical period in the history of agriculture. The new science of bacteriology, just being applied to agriculture, had revealed a new and hitherto completely unexpected world of life—living organisms so small

and yet so numerous that the mind utterly failed to grasp the figures expressing either their size or their number. Astronomy alone could furnish parallels, and men's minds moved in contemplation from the Infinitely Great to the Infinitely Little, lost in wonder and in admiration at the new marvels disclosed by science. In the agricultural laboratories the achievements of Winogradsky, Beijerinck, Warington, and others had shown a wonderful picture of soil life, rousing the imagination and stimulating the scientific interest of many of the younger workers of the day. They had used culture methods, in the main the elective methods, excluding all organisms but the one under investigation and they had achieved marvelous results. Doctor Lipman began also by using these methods to study a question which was then causing considerable commotion in agricultural circles, the loss of nitrogen from farmyard manure. This had always been regarded by practical men as the ideal fertilizer, and the battle of the giants of those days raged about the question: farmyard manure versus artificials. Then farmyard manure was shown to suffer great loss easily, and worse still, to make even artificial fertilizers, especially nitrate of soda, suffer loss also. Great was the perturbation when the German chemists Wagner and Maercker first announced this: Warington at Rothamsted immediately took up the cudgels and showed that the result, as far as farmyard manure was concerned, was obtained only under abnormal conditions never likely to arise in practice. Nevertheless, loss of nitrogen in other ways was sufficiently serious to demand the fullest investigation. The process was called "denitrification" because, being a decomposition of nitrates, it was the reverse of nitrification, and it was soon attributed to bacteria; it was anaerobic and required the presence of organic matter. In studying some of the organisms concerned, Doctor Lipman broached two subjects which have since developed greatly: the importance of joint action or symbiosis of the soil organisms, and the relation between denitrification and the composition of the organic matter concerned, now commonly referred to "as the influence of the carbon/nitrogen ratio," though he did not then put it in that way.

Almost immediately, however, he turned to another subject which had long puzzled scientific workers: Where does the nitrogen of the soil come from? For a hundred years chemists had looked upon nitrogen as the embodiment of inertness, unable to enter into chemical combination or to sustain life: the French, logically minded always, called it "azote"—without life. It was true that some misguided young person had shown how to make it combine with certain metals, forming nitrides, but these compounds, falling outside the recognized lines, were very properly ignored by self-respecting teachers and by the framers of examination syllabuses. Berthelot had suggested that it might be assimilated by certain bacteria but he gave no proof; the idea was regarded as one of those bright thoughts that may be put forward by a man of genius and established reputation, but that need not be taken too seriously. Then, like a bombshell, came Hellriegel and Wilfarth's discoveries that certain micro-organisms associated with leguminous plants certainly could assimilate gase-

ous nitrogen, and finally Winogradsky's and Beijerinck's discoveries of organisms which could fix nitrogen independently of higher plants. Beijerinck's organism was called "Azotobacter," and was particularly interesting. It could not, in his view, find nitrogen by itself—it needed the help of other organisms—but it had the power of setting in train the chain of processes which began with the taking up of nitrogen and ended with the synthesis of protein. Chemists could by this time reproduce the first stage: they could fix nitrogen with the aid of elaborate appliances, high tension electricity, and high temperatures, but they could get no further than nitrate or ammonia, and even yet cannot begin to approach a protein synthesis. Yet here was a lowly organism completing the whole process without appliances, electricity, or extra heat. The organism and the process were alike of fascinating interest and attracted Doctor Lipman from the outset. He isolated, in all, four species—one might more properly say "forms"—of Azotobacter from New Jersey soils and showed also that they could fix nitrogen alone, unaided by other organisms: the power was therefore something inherent in this particular organism. This narrowed down the problem considerably, and others confirmed and extended the work. At the same time he showed that the power of fixation was enhanced by the presence of certain other organisms, one which he labelled "B 30" being a specially efficient partner although in itself unable to fix any appreciable quantity of nitrogen. Not all organisms, however, increased the amount of fixation; some actually depressed it. Again, therefore, he had evidence of the profound effect of joint action. He argued that it is unsafe "to judge of bacterial processes in the soil from a one-sided study of the behavior of single species in certain culture media. Under actual conditions, the modifying influences are very numerous and variable, hence the need of studying carefully not only the *pure* cultures, but also the mixed cultures, but under conditions susceptible of control."

Always practical in his outlook, Doctor Lipman early raised the question: What has all this to do with soil fertility? Are soil microorganisms concerned in the process to any importance? If so, how, and how can we measure their effect? He saw too that a valuable measure, if it could be obtained, would be the rate of ammonification of added organic matter: he could thus obtain information about both soils and organic manures.

For this type of work, however, it was necessary to deal with the soil itself. He thus had the courage to break away from the methods of pure culture and the single organism in spite of the important results they had been giving. He had realized, and he was one of the first to do so, that the soil microorganisms probably form a population, a group with certain permanent, recognizable characteristics, and that the surest way of studying their relation to crop production was to study them in the soil itself. Hence the tumbler method, one of the simplest and most useful methods that could be devised. It gave no startling results, nor was it expected to do so, but it opened the way to much new knowledge about the decomposition processes in the soil and their connection with the growth of plants.

The influence of the composition of organic matter on its rate of decomposition in the soil continued to attract him: in 1907 he pointed out the desirability of adding nitrogen as nitrate after ploughing in green manure in order to hasten the decomposition.

He studied also the relations of bacteria to another element, sulfur. Few people would believe that bacteria could oxidize sulfur to sulfuric acid, but in the New Jersey laboratories it was shown that this actually happened. This found interesting application as a means of controlling soil reaction: it had always been possible to make an acid soil neutral by means of lime, but only one method was known for making a neutral soil acid or an alkaline soil neutral, and that was by prolonged use of sulfate of ammonia without lime. The need for acidification came later into agricultural chemistry; it appeared in two forms: in dry regions to make an alkaline soil neutral, and in wet regions to make a neutral soil intended for potatoes slightly acid so as to put the "scab" organism out of action. The application of sulfur was both practicable and convenient and it has been frequently adopted.

All this time there were continuing at the New Jersey Station the cylinder cropping experiments begun by the late Doctor Voorhees for the purpose of giving some quantitative information about the relative effects of different nitrogenous fertilizers on the more common crops of the region. Doctor Lipman kept up the quantitative form of the experiment; the produce was weighed and analyzed, the soil was periodically tested to see how far in practice the information given by the laboratory methods accorded with the field results. This close linkage of field observation and laboratory experiments has given a special stamp to the New Jersey cylinder investigations, and the data obtained are among the best on their subject. One of the most important deductions from this work is that the value of an organic manure depends not only on the state of combination of its nitrogen but also on its percentage of carbon. A high proportion of carbon tended to increase the number of bacteria and fungi so much that they used up the nitrogen themselves for their own food instead of leaving it as ammonia or nitrate to be taken up by plants. This idea has been extensively developed at New Jersey; it has explained many difficulties met with in field practice, and it helps the expert considerably in his task of assessing the values of the many organic manures now available.

Doctor Lipman's work has always been characterized by originality of outlook. His discovery that *Azotobacter* by itself can fix nitrogen is of historic importance, but equally valuable was his gradual recognition of the importance of the compositions of organic matter—its carbon-nitrogen ratio—on its decomposition in the soil. He also in the course of his work put out many suggestive ideas which others could work up, including the idea of a synthetic agar medium and a suggestion that *Azotobacter* could be used to estimate the available mineral food supplies in the soil: he recognized too, the importance of iron in the nutrition of *Azotobacter*. He exposed at least one false road and showed that it led nowhere—the idea that the nitrogen resources of the soil could be



increased by inoculation with cultures of *Azotobacter*. It had been a simple and attractive idea—men will always fall to the notion of getting something for nothing—but Doctor Lipman was not to be caught; he gave it a fair trial and showed that it was not a way of progress.

As a writer he has the invaluable quality of being able to express himself clearly, and in consequence his books, "Bacteria in Relation to Country Life" and "A Laboratory Guide in Soil Bacteriology" (jointly with P. E. Brown), and his contributions on soil bacteria in relation to soil fertility to Marshall's volume have been widely read.

His influence has not been confined to New Jersey. He was one of the first to recognize the new movement toward world coöperation in science, and he was widely acclaimed as the most suitable person for the presidency of the International Society of Soil Science when that body decided to hold its Congress, the first of the kind, in the United States. So successful was the Congress that the society decided to continue these meetings, and it now affords one of the best examples of the advantages of international coöperation. The movement is only in its infancy: its future is pregnant with possibilities of the greatest significance for the welfare of mankind. The name of Doctor Lipman, the first president, will always be remembered.

Doctor Lipman may well be proud of so great a record of achievements: his friends and colleagues certainly are, and we all unite in wishing him many years more of peaceful happy work at the station to which he has devoted his time, his thought, and his life.





THE CAMPUS OF THE NEW JERSEY AGRICULTURAL EXPERIMENT STATION



# JACOB G. LIPMAN AS AN INVESTIGATOR

## A CHAPTER IN THE HISTORY OF SOIL MICROBIOLOGY

SELMAN A. WAKSMAN

*New Jersey Agricultural Experiment Station*<sup>1</sup>

### INTRODUCTORY

In the history of soil microbiology, the name of Dr. Jacob G. Lipman will always be connected with the study of the cycle of nitrogen in nature, especially the problem of nitrogen fixation by non-symbiotic bacteria, the liberation of nitrogen as ammonia in the process of decomposition of organic nitrogenous substances in soil, and the general relations of nitrogen liberation in soil to the growth of higher plants. His scientific activities began at a time when the importance of microorganisms in soil processes was receiving attention; among these processes none aroused greater interest than the rôle of these organisms in the cycle of nitrogen in nature in general and in the soil in particular. The epoch-making contributions of Winogradsky and Beijerinck were just becoming recognized, and it was Doctor Lipman who represented their school of thought in this country. In order, therefore, to understand the reasons that led him to become actively interested in the rôle of microorganisms in soil processes, it is essential to know the historical development of our knowledge of the science of the soil and its relation to agriculture in general and in this country in particular, at the time Doctor Lipman first entered the field of scientific research.

The last two decades of the nineteenth century marked the beginning of a new science, that of the bacteria in the soil. Minute microscopic organisms have become recognized as important agents not only in disease and numerous fermentations but also in the soil, taking part in a number of transformations that are essential for plant development. It was discovered that the soil was not an inert mass of inorganic compounds and of dead organic residues, but was teeming with life. The microscopic organisms which were found to inhabit the soil were shown to comprise numerous groups having highly specialized functions and participating in numerous soil processes. Among the outstanding contributions which loomed large and which have since become classics in the science of soil bacteriology, it is sufficient to mention the work of Robert Koch (1881) on the plate method, whereby it was made possible to determine the abundance of bacteria in the soil, and the investigations of Hellriegel and Wilfarth, Beijerinck, Schloesing, and Laurent on the rôle of bacteria in the

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

fixation of nitrogen by leguminous plants. The extensive and painstaking studies of French, German, and English investigators on the agents responsible for the process of nitrification in soil culminated in the brilliant contributions of Winogradsky, who succeeded in isolating the nitrifying bacteria in 1891. This achievement was followed, in 1893, by his isolation of the first group of non-symbiotic nitrogen-fixing organisms, the anaerobic *Clostridium pastorianum*. Our knowledge of the process of ammonia liberation in soil through the decomposition of nitrogenous organic complexes by microorganisms had been enriched and firmly established by the work of Marchal and of Müntz and Coudon, in 1893.

Soon after it became evident that various specific bacteria are concerned with highly beneficial soil processes, Wagner announced (in 1895) that certain soil bacteria may also bring about extensive losses of nitrogen from the soil; when nitrates are introduced into the soil together with stable manures, they are rapidly destroyed, giving rise to gaseous nitrogen. Although the existence in the soil of bacteria capable of reducing nitrates (denitrification) was known during the previous decade, the rapidly increasing application to soils of inorganic fertilizers, especially of nitrates as nitrate of soda, immediately centered the attention of the scientific world upon this process as a possible danger to the most efficient utilization of nitrogen by growing crops. This claim of Wagner aroused considerable interest among the agricultural institutions in the United States and led directly to the establishment at the New Jersey Station of the first research project dealing with the bacterial population of the soil. The New Jersey Agricultural Experiment Station under the leadership of Doctor E. B. Voorhees, director and chief chemist, was already engaged in extensive studies on the influence of fertilizers, especially nitrogenous salts, upon plant growth. It was, therefore, logical that the study of the utilization of different fertilizers should lead directly to a study of the transformation of these compounds in the soil. In 1898, a series of investigations were begun on the changes that nitrogen undergoes in the soil; John P. Street was then appointed as associate chemist, to assist Doctor Voorhees in these studies. The very first experiments dealt with the reduction of nitrates in the soil, with the changes produced in the nitrogen in barnyard manure, and with the availability of the nitrogen in the liquid and solid portions of the manure, as compared with inorganic salts as sources of nitrogen for plant growth.

The 20th Annual Report of the Experiment Station, for the year ending October 31, 1899, contains a paper by Street (p. 86) on "The Reduction of Nitrates in the Presence of Barnyard Manure" and a contribution by Voorhees (p. 97) on "Investigations Relative to the Use of Nitrogenous Materials." These investigations were continued during the following two years, and the results were published in the 21st and 22nd Annual Reports of the New Jersey Station, which appeared October 31, 1900 and 1901 respectively. The latter report contains a paper entitled "A Review of the Investigations Concerning

Denitrification," in which a summary is presented of the current ideas in Europe and in this country on the reduction of nitrates in the soil.

In these first investigations, special emphasis was laid upon the chemical processes and upon the response of the growing plant. They were sufficient, however, to convince Doctor Voorhees that it was highly essential, in order to understand these processes, also to undertake a study of the microorganisms responsible for them, especially in connection with the cycle of nitrogen. A recent graduate of Rutgers College (Class of 1898) who was then carrying out graduate work in bacteriology at Cornell University, namely, Jacob G. Lipman, was invited to undertake these investigations, and, on July 1, 1901, he received the appointment of assistant in soil chemistry and bacteriology at the New Jersey Station. This appointment was made for the special purpose of studying "the movement of plant food in the soil, and the part of bacteria in the formation, change or destruction of such plant food."

The new assistant immediately set to work upon the problem assigned to him. Fresh from his work at Cornell University on methods of studying bacteria in general, he applied the information thus gained to the bacteria of the soil. His first investigation was reported the same year, in the form of a two-page paper published in the 22nd Annual Report of the Station (1901, p. 213-214). It described a sampling tube for taking adequate soil samples for bacteriological work. One year later, an extensive paper (23rd Annual Report for 1902, N. J. Agr. Exp. Station, p. 183-241) dealing with the morphology and physiology of denitrifying bacteria was published. This first important contribution of Doctor Lipman to the subject of the bacterial population of the soil and its relation to soil fertility shows a firm grasp of the literature, a critical attitude toward the subject under investigation, and an original method of approach. Several new cultures of bacteria were isolated and described. This paper, however, also tended to indicate that the problem of denitrification was not absorbing all the interest of the young investigator, but that another problem, namely, that of the bacteria concerned in the process of non-symbiotic nitrogen-fixation was also attracting his interest. This is shown by the fact that some consideration is given to this subject, even in this first paper, since a certain phase of the investigation deals with "The Fixation of Nitrogen by Denitrifying Bacteria."

#### THE FIRST PERIOD, 1902-1911

Probably one of the most important scientific contributions, if not the most important contribution, ever made by Doctor Lipman is found in his second paper, published as the Report of the Assistant in Soil Chemistry and Bacteriology in 1903 (24th Annual Report, p. 217-285). This paper deals with "Experiments on the Transformation and Fixation of Nitrogen by Bacteria." A brief description of a newly isolated non-symbiotic nitrogen-fixing organism, *Azotobacter vinelandii*, as well as a preliminary description of several other organisms, was given. This material comprised a part of the thesis presented

in 1903 for the degree of doctor of philosophy at Cornell University. This work followed immediately upon the discovery by M. W. Beijerinck (1901) of the first aerobic non-symbiotic organism, *Azotobacter chroococcum*. This group of organisms, comprising the genus *Azotobacter*, has since become recognized as one of the most important members of the soil population. Although Beijerinck was the first to isolate a representative of this group, he did not recognize the fact that this organism can fix large quantities of nitrogen in the absence of any other bacteria. Lipman not only isolated the second important member of the group, but he was also among the first to prove beyond any doubt that these bacteria are capable of fixing large quantities of nitrogen obtained from the atmosphere, even in pure culture, using various forms of carbon as sources of energy.

The following year marks the promotion of Doctor Lipman at the New Jersey Station from the position of assistant to that of soil chemist and bacteriologist. The report of the investigations carried out during the year ending October 31, 1904 (25th Annual Report, p. 237-285) contains his paper "Further Contributions to the Physiology and Morphology of Members of the *Azotobacter* Group." This report is preceded by a detailed survey of the status of soil bacteriology in general. Two new species of *Azotobacter* are described; namely, *Az. Beijerinckii* and *Az. Woodstownii*. A detailed study is now presented of the physiological activities of the genus *Azotobacter*. The investigation of the influence of reaction upon growth of this organism revealed the fact that the negative results previously obtained by Beijerinck concerning the ability of *Azotobacter* to fix nitrogen in pure culture were directly due to the acidity of the medium employed by Beijerinck. When the medium was properly buffered, positive fixation was definitely obtained. The first thermochemical considerations of the mechanism of nitrogen fixation are also found in this paper. An attempt was made to inoculate the soil with *Azotobacter*, but the results obtained were entirely negative: no gain in nitrogen could be demonstrated in the case of the inoculated soil. It should be noted here that this particular problem is still receiving considerable attention, and the information thus gained during the last three decades has not greatly advanced knowledge of the subject.

Although the aforementioned investigations were continued also during the following year, as shown by the results published in the 26th Annual Report (1905, p. 233-280), a new approach to the subject of soil bacteriology could then be definitely observed, namely an attempt to measure the fertility of the soil from determinations of nitrogen changes. Considerable attention was then being paid to the production of ammonia during the decomposition of proteins and other organic nitrogenous compounds in the soil. This new phase of bacteriology was gradually replacing the previous interest in the problem of nitrogen-fixation. A study was undertaken of the fertility of different soils, as measured by their crop yields, in cylinders and in field plots. The results thus obtained were compared with the ammonifying power of the same



soils, as measured by the formation of ammonia upon addition of nitrogenous organic compounds.

Just as the studies of the process of non-symbiotic nitrogen fixation followed directly the work of Winogradsky and Beijerinck on the same subject, investigations of ammonia-formation in the process of decomposition of organic matter in soil and the study of the rate of "ammonification" as an index of the productive capacity of the soil, followed directly the work of Remy. Löhnis in Germany and Lipman in this country may be considered as the first and most outstanding representatives of the "ammonification" studies carried out in Europe and in America, respectively. These two bacteriologists became the outstanding leaders in the investigation of several distinct soil microbiological processes; namely, ammonification, nitrification, nitrogen-fixation, and denitrification. The results obtained in these studies were believed to indicate that measurements of the biological condition of the soil could serve as a reliable guide to the productive capacity of the soil. The period of 1904-1905 can, therefore, be considered as one of interest, not only in the development of soil bacteriology at the New Jersey Station, but in the world as a whole.

The following year (27th Annual Report 1906, p. 119-188) was devoted practically entirely to ammonification studies. Soils of different origin as well as the same type of soil under different systems of fertilization were compared in ability to produce ammonia from various organic compounds. Ammonia formation by pure cultures of bacteria, especially *Bac. mycoides*, was also studied. Particular attention should be called here to one investigation carried out that year which may be considered as the direct forerunner of the now popular Azotobacter method for determining the presence and abundance of available minerals in soil. This method is based upon the ability of Azotobacter to grow in a solution containing an adequate supply of energy with the particular soil as the only source of one specific nutrient element. This method was later developed extensively by Christensen in Denmark and is at present applied on a large scale in Europe by Niklas and others, without sufficient credit being given, however, to its originator. The Annual Report for 1906 definitely states: "It would seem . . . that nitrogen-fixing bacteria of the Azotobacter type, which are largely independent of the supply of combined nitrogen in the soil, could be made to grow in mannite or dextrose solutions devoid of any mineral nutrients, but provided with quantities of sterile soil. Theoretically, it would also appear that the development of the Azotobacter organisms, and the accompanying fixation of nitrogen, should be in proportion to the amount of mineral nutrients supplied by the sterile soil." The results obtained from a series of investigations showed that "everything being equal, bacterial growth will be determined by the rate of solution of the mineral nutrients, and particularly of the soil phosphates." Those soils which contained the largest amount of phosphates in an available form allowed the most vigorous development of the bacteria and, as a result of this, also of the amount of nitrogen fixed. "There was proportionately and absolutely more Azotobac-

ter growth in the mannite solution containing larger amounts of phosphates of greater initial solubility."

In 1907 P. E. Brown, a student at Rutgers, was appointed assistant chemist, and for several years, contributions from the Station to the subject of soil bacteriology were under the joint authorship of Lipman and Brown. The next paper (28th Annual Report, p. 141-204) contains a continuation of the investigations on the ammonifying capacity of the soil. An abnormal soil from Madison, Wisconsin, was studied in great detail; it was found that the unfavorable soil conditions could be corrected by treatment of the soil with carbon bisulfide; the improvement in the productive capacity of the soil was found to run parallel with an increase in the ammonifying, nitrifying, and nitrogen-fixing capacities and with a decrease in the denitrifying capacity of the soil. Further studies of the inoculation of soil with *Azotobacter* led, again, to definite conclusions that this alone did not bring about any increase in the nitrogen resources of the soil. The organism could not survive in soils which did not offer suitable conditions for its growth. An important contribution appeared in 1907, in the form of a joint paper with Doctor E. B. Voorhees and published as Bulletin 194 of the Office of Experiment Stations under the title "A Review of Investigations in Soil Bacteriology." This paper presented a detailed summary of the subject of the bacteriology of the soil and was at that time as complete a review of this subject as had ever been made available in the English language.

Various investigations dealing with ammonification, nitrification, and nitrogen-fixation in soil and in artificial culture media were continued during the following year (29th Annual Report, 1908, p. 95-147); however, new lines of attack of the soil microbiological complex were begun that year. Among the most important problems considered were the study of the influence of dextrose and other carbohydrates upon the biological activities in soil, as measured by ammonification of peptone, urea, and gelatin, as well as by bacterial multiplication; the utilization of the soil or tumbler method, as compared with the solution method, for the study of bacteriological activities in soil; and a comparative study of methods and culture media for measuring bacterial activities and bacterial numbers in soil. These investigations, although following in the course of logical development of the previous studies, marked important steps in the advance of the subject of soil bacteriology. A comparative study of different media for the determination of abundance of bacteria in soil resulted in the development of a synthetic agar medium which gave considerably larger numbers of bacteria than did the common bouillon agar previously employed; it was also standard in composition and, consequently, could be easily duplicated without affecting bacterial development. The same year witnessed the publication by Lipman of the now well-known book "Bacteria in Relation to Country Life" (MacMillan Co., New York, 1908). Although this book has never gone into a second edition, it was reprinted a number of times and was used extensively in colleges and in schools, as well as by farmers and county

agents; it has contributed materially to the dissemination of correct information concerning the rôle of bacteria in agriculture in general and in soil science in particular.

During the following two years (30th Annual Report, 1909, p. 117-222; 31st Annual Report, 1910, p. 89-182) the solution methods for the study of soil bacteriological processes were completely abandoned; their place was taken by the tumbler or soil methods, especially for the study of ammonification and nitrification. A detailed investigation of the influence of chemical, physical, and mechanical soil properties on the process of ammonification was also carried out. The relative availability of organic nitrogenous materials was determined by the rate of their transformation in the soil into ammonia and nitrate. It was demonstrated that in the decomposition of materials of plant origin containing only a small percentage of nitrogen the relatively abundant supply of carbohydrates leads to an extensive development of fungi and bacteria; these use up the nitrogen for the production of microbial cell substance. The carbon-nitrogen ratio of an organic material undergoing decomposition was found to be an important factor in influencing the rate of liberation of the nitrogen in an available form. The results of these investigations led to the suggestion that knowledge of the carbon-nitrogen ratio of organic matter is essential for an understanding of the availability of the nitrogen in the organic substances added to the soil.

The peak of investigations in soil bacteriology carried out directly by Doctor Lipman was reached in 1911. That year, his major assistant, P. E. Brown, left the station to assume an important position in the field of soil bacteriology at the Iowa Experiment Station, and several new members were added to the staff of the New Jersey Station; notably, A. W. Blair, who was to assist for many years to come in carrying out the field studies as well as the chemical investigations of the soil, and H. C. McLean, who was to devote his time largely to the soil bacteriological investigations. The Department of Soil Chemistry and Bacteriology (32nd Annual Report, 1911, p. 159-267) continued its investigations of the availability of nitrogenous materials in soil, as measured by the ammonification process, and of the influence of stable manure, nitrate of soda, and various stimulants on ammonification. Studies of the influence of protozoa and of soil pasteurization on ammonification continued for many years at the Station. An interesting attempt was made that year (*Bot. Gaz.* 51: 454-460, 1911) to systematize the terminology of soil bacteriological processes. A number of new terms to define certain established soil processes were suggested. Some of these, such as "azofication," "sulfofication," "ferrification," have since found a limited application in soil bacteriological literature; however, many others were proposed, which have never been used. Doctor Lipman published, during the same year, "A Laboratory Guide in Soil Bacteriology" (with P. E. Brown as joint author) and several chapters on "Soil Bacteria in Relation to Soil Fertility" in Marshall's *Microbiology*. Both of these proved useful for many years to students and investigators as sources of information concerning soil bacteria and their rôle in soil processes.

The decade from 1901 to 1911 resulted in a series of brilliant contributions by Doctor Lipman to our understanding of the rôle of bacteria in soil processes, especially in nitrogen-fixation and in decomposition of plant and animal residues added to the soil. His research activities, however, were not limited to the bacteria of the soil; these years were also marked by extensive field studies and by a growing interest in soil fertility problems.

#### THE SECOND PERIOD, 1911—

The appointment of Doctor Lipman to the directorship of the New Jersey Station in 1911 prevented him from carrying out further the investigations on soil chemistry and bacteriology. He has continued, however, to supervise, guide, assist, and stimulate his associates and the large number of graduate students and assistants who have gathered around him to receive their training in the field of soil bacteriology. Many of the investigations carried out since 1911 were either initiated directly by Doctor Lipman or begun at his suggestion. It is sufficient to call attention to some of these problems.

*The occurrence of protozoa in soil and their rôle in soil processes.* The theory proposed (1909–1913) by Russell and Hutchinson at the Rothamsted Station that the protozoa of the soil keep bacterial development in check and that the favorable effect of partial sterilization upon soil fertility is due to the destruction of protozoa aroused considerable interest. Doctor Lipman and his associates undertook a series of systematic investigations on the occurrence of protozoa in soil and their relations to bacteria and to soil processes. The results obtained pointed to the great abundance of protozoa in soil; they tended to modify the earlier conception, however, that protozoa exert a controlling effect upon soil processes.

*The rôle of bacteria in the oxidation of sulfur and the transformation of insoluble phosphates into soluble forms.* It was found that as a result of composting sulfur, rock phosphate, and soil, the sulfur became oxidized to sulfuric acid and the latter interacted with the phosphate to render it soluble. This process was biological in nature, since when a fresh compost was inoculated with some material from an older compost, the processes began to take place much more rapidly. A detailed study of the organisms concerned in the process finally resulted in the isolation of a highly active sulfur-oxidizing bacterium, later named *Thiobacillus thiooxidans*.

*Continuation of field, cylinder, and pot experiments.* These consisted in such studies as the availability of different nitrogenous fertilizers, a comparison of organic and inorganic fertilizers, the influence of lime upon crop production, and factors influencing protein content of legumes.

In addition to these three major fields of investigation, a number of other problems in soil chemistry and bacteriology received more or less attention, such as the influence of bacteria supplied in the stable manure upon the decomposition of the organic matter added to soil, especially green manures; the influence of ferrous sulfate and gypsum on crop yield and nitrogen recovery;

the associative growth of legumes and non-legumes; the formation of carbon dioxide and nitrates in the presence of large amounts of carbohydrates. These studies led to several important new lines of attack of the chemical and bacteriological soil problems, begun by associates and students of Doctor Lipman under his direct and indirect supervision. The problem of oxidation of sulfur in soil resulted in detailed studies on the use of this process for the transformation of insoluble phosphates into soluble forms. These investigations were directly responsible for a more scientific use of sulfur in agriculture. Among the practical applications it is sufficient to mention: 1, the control of the soil reaction: a specific acid reaction suppressing the development of certain plant pathogens, notably the organism causing potato scab; 2, the control of the alkalinity in "black-alkali" soils. The investigations on the soil population led later to extensive studies of soil fungi, soil protozoa, and soil actinomycetes and of their rôle in soil processes.

Doctor Lipman's contributions to soil science have had a marked effect upon the further development of this subject, particularly soil microbiology and soil chemistry, especially in this country. His contributions to our knowledge of the problem of *non-symbiotic nitrogen fixation* and of the *decomposition of organic matter with the liberation of nitrogen in an available form* can be considered the most original and important results in his investigations. If he had done nothing more, his place as an investigator in the field of soil science would be assured. Add to that his important contributions to our knowledge of the fertilizer requirements of plants and of the rôle of microorganisms in soil processes, and one will readily appreciate the value of his work in advancing the theoretical and applied phases of soil science.

Doctor Lipman's investigations came within a period of historical development of soil microbiology when both scientists and practical agriculturists were asking for applications of this science to agriculture. His work falls during a period of transition between the science developed in the laboratory and the application of the results thus obtained to field conditions. He contributed to both and thus helped to carry the science through one of the most difficult periods of its development. He has not only helped to advance the science of the soil, but also to digest and interpret it and to point to the applications of the science to practical agriculture. His contributions to agriculture in general and to soil science in particular are far from ended. This is evidenced by the fact that he is utilizing the sabbatical year granted to him by the Trustees of the College and Station, to complete a monumental work on the plant food resources of the United States.

#### SELECTED LIST OF SCIENTIFIC PUBLICATIONS OF JACOB G. LIPMAN

- 1902 Studies in Nitrification. *Journal American Chemical Society* 24: 171-186.
- 1902 The Individuality of Plants as Important Factor in Plant Nutrition Studies. (Joint author with E. B. Voorhees). *Proceedings 23rd Annual Meeting Society for Promotion of Agricultural Science* 1902: 42-49.
- 1903 The Fixation of Atmospheric Nitrogen by Bacteria. *Proceedings 20th Annual Convention of Association Official Agricultural Chemists*, Washington, D. C., 1903.

- 1905 Experiments on the Accumulation and Utilization of Atmospheric Nitrogen in the Soil. (Joint author with E. B. Voorhees). *Journal American Chemical Society* 27: 556.
- 1905 Report on Tests of Cultures for Soil Inoculation. *New York (Geneva) Agricultural Experiment Station Bulletin* 270.
- 1905 Experiments on the Accumulation and Utilization of Atmospheric Nitrogen in the Soil. (Joint author with E. B. Voorhees). *New Jersey Agricultural Experiment Station Bulletin* 180.
- 1907 Losses of Ammonia from Culture Solutions. *Journal American Chemical Society* 29: 1358-1362.
- 1907 Some Chemical Bacteriological Effects of Liming. (Joint author with P. E. Brown). *New Jersey Agricultural Experiment Station Bulletin* 210.
- 1908 Inoculation Experiments with Azotobacter, Bacteriological Studies in Madison Soil, Ammonification in Culture Solutions as Affected by Soil Treatment. *Centralblatt für Bakteriologie*, etc. (II): 541-542.
- 1908 Sandy Soils and Their Improvement in the Growing of Forage Crops. (Joint author with E. B. Voorhees). *New Jersey Agricultural Experiment Station Bulletin* 211.
- 1908 *Bacteria in Relation to Country Life*. The MacMillan Co., New York.
- 1909 Experiments on the Utilization of Nitrogen in Fertilizer Materials. *Journal of Industrial and Engineering Chemistry* 1: 397-408.
- 1909 Media for the Quantitative Estimation of Soil Bacteria. (Joint author with P. E. Brown). *Centralblatt für Bakteriologie*, etc. (II) 25: 447.
- 1909 Methods Relating to the Rate of Decomposition of Organic Matter in the Soil. Proceedings 25th Annual Convention Association of Official Agricultural Chemists, Washington, D. C., 1909. *U. S. Department of Agriculture, Bureau of Chemistry, Bulletin* 122.
- 1909 Investigations Relative to the Use of Nitrogenous Materials, 1898-1907. (Joint author with E. B. Voorhees). *New Jersey Agricultural Experiment Station Bulletin* 221.
- 1910 Some Bacteriological Relations in Soils Kept Under Greenhouse Conditions. (Joint author with I. L. Owen). *Journal of Agricultural Science* 3: 305.
- 1910 Bacteriological Methods for Determining the Available Nitrogen in Fertilizers. *Journal of Industrial Engineering Chemistry* 2: 146-148.
- 1910 Experiments on Ammonia and Nitrate Formation in Soils. (Joint author with P. E. Brown). *Centralblatt für Bakteriologie*, etc. (II) 26: 590.
- 1910 A Method for the Study of Soil Fertility Problems. *Journal of Agricultural Science* 3: 299-300.
- 1910 Tests of Commercial Cultures for Soil Inoculation. *New Jersey Agricultural Experiment Station Bulletin* 227.
- 1911 The Relation of Nitrate of Soda to the Mechanical Condition of Commercial Fertilizers. *Journal of Industrial and Engineering Chemistry* 3: 655-657.
- 1911 Bacteriological Methods for the Estimation of Soil Acidity. *Science* 33: 971-973.
- 1911 The Availability of Nitrogenous Materials as Measured by Ammonification. (Joint author with P. E. Brown and I. L. Owen). *Centralblatt für Bakteriologie*, etc. (II) 31: 49.
- 1911 Experiments on Ammonia and Nitrate Formation in Soils. (Joint author with P. E. Brown and I. L. Owen). *Centralblatt für Bakteriologie*, etc. (II) 30: 150.
- 1911 The Biological Factor in Soil Investigation. *Proceedings of the Society for the Promotion of Agricultural Science*, 1911.
- 1911 Conditions Affecting the Availability of Nitrogen Compounds in Vegetation Experiments. (Joint author with A. W. Blair, I. L. Owen, and H. C. McLean). *New Jersey Agricultural Experiment Station Bulletin* 249.
- 1911 *A Laboratory Guide in Soil Bacteriology*. (Joint author with P. E. Brown). Published by authors.

- 1912 Observations on Soil Inoculation. *Proceedings of the Society for the Promotion of Agricultural Science* 1912: 69-75.
- 1912 Factors Relating to the Availability of Nitrogenous Plant-Foods. (Joint author with A. W. Blair, I. L. Owen, and H. C. McLean). *Proceedings Eighth International Congress of Applied Chemistry*.
- 1912 The Availability of Nitrogenous Materials as Measured by Ammonification. (Joint author with A. W. Blair, I. L. Owen, and H. C. McLean). *New Jersey Agricultural Experiment Station Bulletin* 246.
- 1912 Experiments on Ammonia Formation in the Presence of Carbohydrates and of other Non-Nitrogenous Organic Matter. (Joint author with A. W. Blair, I. L. Owen, and H. C. McLean). *New Jersey Agricultural Experiment Station Bulletin* 247.
- 1912 Experiments Relating to the Possible Influence of Protozoa on Ammonification in the Soil. (Joint author with A. W. Blair, I. L. Owen, and H. C. McLean). *New Jersey Agricultural Experiment Station Bulletin* 248.
- 1912 Conditions Affecting the Availability of Nitrogen Compounds in Vegetation Experiments. (Joint author with A. W. Blair, I. L. Owen, and H. C. McLean). *New Jersey Agricultural Experiment Station Bulletin* 249.
- 1912 Miscellaneous Vegetation Experiments. (Joint author with A. W. Blair, I. L. Owen, and H. C. McLean). *New Jersey Agricultural Experiment Station Bulletin* 250.
- 1912 Factors Relating to the Availability of Nitrogenous Plant Foods. (Joint author with A. W. Blair, I. L. Owen, and H. C. McLean). *New Jersey Agricultural Experiment Station Bulletin* 251.
- 1912 The Associative Growth of Legumes and Non-Legumes. *New Jersey Agricultural Experiment Station Bulletin* 253.
- 1912 Conditions Affecting the Availability of Nitrogen Compounds in Vegetation Experiments. (Joint author with A. W. Blair, I. L. Owen, and H. C. McLean). *New Jersey Agricultural Experiment Station Bulletin* 257.
- 1912 Experiments on the Accumulation and Utilization of Atmospheric Nitrogen in Field Soils. (Joint author with A. W. Blair, I. L. Owen, and H. C. McLean). *New Jersey Agricultural Experiment Station Bulletin* 258.
- 1913 Field Experiments on the Availability of Nitrogenous Fertilizers. (Joint author with A. W. Blair). *New Jersey Agricultural Experiment Station Bulletin* 260.
- 1914 Comparison of Magnesians and Non-Magnesian Limestone in Rotation Experiments. (Joint author with A. W. Blair, H. C. McLean, and L. F. Merrill). *New Jersey Agricultural Experiment Station Bulletin* 267.
- 1914 Nitrogen Utilization in Field and Cylinder Experiments. (Joint author with A. W. Blair, H. C. McLean, and L. F. Merrill). *New Jersey Agricultural Experiment Station Bulletin* 268.
- 1914 Methods and Results in Vegetable Experiments. (Joint author with A. W. Blair). *New Jersey Agricultural Experiment Station Bulletin* 269.
- 1914 Pot Experiments on the Availability of Nitrogen in Mineral and Organic Compounds. (Joint author with A. W. Blair, H. C. McLean, and L. K. Wilkins). *New Jersey Agricultural Experiment Station Bulletin* 280.
- 1914 Nitrogen Utilization in Field and Cylinder Experiments. II. (Joint author with A. W. Blair, H. C. McLean, and L. K. Wilkins). *New Jersey Agricultural Experiment Station Bulletin* 281.
- 1914 Factors Influencing the Protein Content of Soy Beans. (Joint author with A. W. Blair, H. C. McLean, and L. K. Wilkins). *New Jersey Agricultural Experiment Station Bulletin* 282.
- 1916 Factors Influencing the Protein Content of Soy Beans. (Joint author with A. W. Blair). *Soil Science* 1: 171-178.
- 1916 The Oxidation of Sulfur in Soils as a Means of Increasing the Availability of Mineral Phosphates. (Joint author with H. C. Lint and H. C. McLean). *Soil Science* 1: 533-539.

- 1916 The Yield and Nitrogen Content of Soy Beans as Affected by Inoculation. (Joint author with A. W. Blair). *Soil Science* 1: 579-584.
- 1916 Sulfur Oxidation in Soils and its Effect on the Availability of Mineral Phosphates. (Joint author with H. C. McLean and H. C. Lint). *Soil Science* 2: 499-538.
- 1916 Investigations Relative to the Use of Nitrogenous Plant-Foods, 1898-1902. (Joint author with A. W. Blair). *New Jersey Agricultural Experiment Station Bulletin* 288.
- 1916 Cylinder Experiments Relative to the Utilization and Accumulation of Atmospheric Nitrogen. (Joint author with A. W. Blair). *New Jersey Agricultural Experiment Station Bulletin* 289.
- 1917 The Yield and Nitrogen Content of Soy Beans as Influenced by Lime. (Joint author with A. W. Blair). *Soil Science* 4: 71-77.
- 1917 Vegetation Experiments on the Availability of Treated Phosphates. (Joint author with H. C. McLean). *Soil Science* 4: 337-343.
- 1917 The Influence of Lime Upon the Yield of Dry Matter and Nitrogen Content of Alfalfa. *New Jersey Agricultural Experiment Station Bulletin* 316.
- 1918 Experiments with Sulfur-Phosphate Composts Conducted under Field Conditions. (Joint author with H. C. McLean). *Soil Science* 5: 243-250.
- 1918 Twenty Years' Work on the Availability of Nitrogen in Nitrate of Soda, Ammonium Sulfate, Dried Blood and Farm Manures. (Joint author with A. W. Blair). *Soil Science* 5: 291-301.
- 1918 The Effect of Liming on Crop Yields in Cylinder Experiments. (Joint author with A. W. Blair). *Soil Science* 6: 5-25.
- 1918 The Lime Factor in Permanent Soil Improvement, I. Rotations without Legumes, II. Rotations with Legumes. (Joint author with A. W. Blair). *Soil Science* 9: 83-90, 91-114.
- 1918 The Value of Nitrate of Soda in Crop Production. (Joint author with A. W. Blair). *New Jersey Agricultural Experiment Station Bulletin* 323.
- 1918 Our Fertility Resources as Bearing on the Present Emergency. *New Jersey State Department of Agriculture Bulletin* 11.
- 1920 Field Experiments on the Availability of Nitrogenous Fertilizers, 1908-1917. (Joint author with A. W. Blair). *Soil Science* 9: 371-392.
- 1920 The Influence of Initial Reaction on the Oxidation of Sulfur and the Formation of Available Phosphates. (Joint author with J. S. Joffe). *Soil Science* 10: 327-332.
- 1920 Some of the New Applications of Sulfur in Agriculture. *Chemical Age* 28: 234-235.
- 1921 Inoculated Sulfur as a Plant-Food Solvent. (Joint author with A. W. Blair, W. H. Martin, and C. S. Beckwith). *Soil Science* 11: 87-92.
- 1921 Nitrogen Losses under Intensive Cropping. (Joint author with A. W. Blair). *Soil Science* 12: 1-19.
- 1921 The Influence of Varying Amounts of Sulfur in the Soil, on Crop Yields, Hydrogen-ion Concentration, Lime Requirement and Nitrate Formation. (Joint author with A. L. Prince and A. W. Blair). *Soil Science* 12: 197-207.
- 1921 The Oxidation of Sulfur by Soil Microorganisms. (Joint author with S. A. Waksman and J. S. Joffe). *Soil Science* 12: 475-489.
- 1921 The Value of Liming in a Crop Rotation With and Without Legumes. *Journal of the American Society of Agronomy* 13: 206-210.
- 1921 A Comparative Study of the Value of Nitrate of Soda, Leguminous Green Manures and Stable Manure in Cylinder Experiments, 1907-1919. (Joint author with A. W. Blair). *Journal of Agricultural Science* 11: 323-336.
- 1922 L'Industrie des Engrais aux Etats-Unis. *Chimie et Industrie* 7: 1001-1008.
- 1923 Recent Investigations on the Oxidation of Sulfur by Microorganisms. *Industrial and Engineering Chemistry* 15: 404.



- 1923 A Comparison of Magnesian and non-Magnesian Limestone in some Five-Year Rotations. (Joint author with A. W. Blair, H. C. McLean and A. L. Prince). *Soil Science* 15: 307-328.
- 1923 The oxidation of Selenium by a New Group of Autotrophic Microorganisms. (Joint author with S. A. Waksman). *Science* 57: 60.
- 1923 Tendencies in Agricultural Research. *Science* 57: 71-76.
- 1924 The Utilization of Nitrogen in Soils and Fertilizers as Affected by Lime. (Joint author with A. W. Blair). *Industrial and Engineering Chemistry* 16: 373.
- 1924 The Value of Sulfur in Soil Improvement and Crop Production. *Industrial and Engineering Chemistry* 16: 250-252.
- 1924 Edaphics (soils research). *Journal of the American Society of Agronomy* 16: 627-632.
- 1925 Field Experiments on the Availability of Nitrogenous Fertilizers, 1918-1922. (Joint author with A. W. Blair and A. L. Prince). *Soil Science* 19: 57-79.
- 1925 The Agricultural Value of Some of the Newer Nitrogenous Fertilizers. (Joint author with H. C. McLean). *Industrial and Engineering Chemistry* 17: 190.
- 1925 The Fixation of Nitrogen under Field Conditions. *Journal of the American Society of Agronomy* 17: 450-455.
- 1925 Organic Evolution from the Point of View of the Soil Investigator. *Scientific Monthly* 21: 310-312.
- 1926 The Effect of Lime and Fertilizers on the Potash Content of Soil and Crop. (Joint author with A. W. Blair and A. L. Prince). *Proceedings of the International Society of Soil Science* 2: 201-208.
- 1926 Future Trends in Soil Conservation. *Industrial and Engineering Chemistry* 18: 1034-1040.
- 1926 Bacteria Concerned in the Oxidation of Sulfur in the Soil. (Joint author with S. A. Waksman). *Proceedings of the 4th International Soil Science Conference* (1924) 3: 240-246.
- 1927 The Nitrogen Problem in Agriculture. *Journal of Chemical Education* 4: 845-860.
- 1927 Factors of Significance in the Development of European Agriculture. *Science* 65: 51-53.
- 1927 Soils and Men. *Proceedings and Papers of the 1st International Congress, Soil Science* 1: 18-24.
- 1927 Microbiological Aspects of Green Manuring. (Joint author with A. W. Blair). *Proceedings and Papers of the 1st International Congress, Soil Science* 3: 312-316.
- 1927 The Influence of Manure, Commercial Fertilizers, and Lime on the Chemical Composition of Field Soils. (Joint author with A. W. Blair and A. L. Prince). *Proceedings and Papers of the 1st International Congress, Soil Science* 3: 454-464.
- 1928 Micro-organisms in Relation to Soil Fertility. Chapter in *The Newer Knowledge of Bacteriology and Immunology*. Edited by E. O. Jordan and I. S. Falk. (University of Chicago, 1928). P. 341-350.
- 1928 Field Experiments on the Availability of Nitrogenous Fertilizers, 1923-1927. (Joint author with A. W. Blair and A. L. Prince). *Soil Science* 26: 1-25.
- 1929 The Fertilization and Management of Grasslands. *Journal of the American Society of Agronomy* 21: 19-28.



## JACOB G. LIPMAN AND NEW JERSEY AGRICULTURE

A. W. BLAIR

*New Jersey Agricultural Experiment Station<sup>1</sup>*

While Doctor Lipman was still a student at Rutgers College, his determination to conquer difficult situations betokened his future contributions to New Jersey agriculture. He has told how, beginning in his freshman year, he would rise at 4 o'clock in the morning to assist with the milking of the College Farm herd. His college day over, he would return to the farm, which was more than a mile from the college campus, to do his share of the evening milking. It is this indomitable spirit that has brought to him national and international recognition in the field of agriculture, particularly in soil science. He was not afraid of hard work in his college days, and this habit of hard work has grown as the years have gone by.

He early realized that to be of value to agriculture in New Jersey, or anywhere else for that matter, he must thoroughly master all phases of the problem. He therefore set himself the task of gaining knowledge in all the sciences related to agriculture. He studied the geological origin of soil and its chemical, physical, and biological properties—how plants grow and get their nourishment; the care and feeding of animals; the marketing of crops; the economic problems which confront the farmer; and many other subjects.

He was fortunate, indeed, in having as his teacher and later as his chief Dr. E. B. Voorhees, who was professor of agriculture in Rutgers and director of the Agricultural Experiment Station. Although Doctor Lipman received guidance and inspiration from Doctor Voorhees, nevertheless, he showed determination to do his own work and to advance only as his record of work entitled him to advancement.

Just as Doctor Lipman began his work as assistant chemist in the Experiment Station, Doctor Voorhees was inaugurating his famous cylinder experiments for the study of nitrogen availability and nitrogen gains and losses in the soil. Doctor Lipman developed this work, and his results in this field are known throughout the world, wherever there are agricultural experiment stations. His keen intellect and his knowledge of foreign languages enabled him to find out quickly what had been done by other workers on any problem that he was studying.

Among his early experiments should be mentioned those on the improvement of the poor sandy soils in certain sections of southern New Jersey. By these experiments he definitely showed that through the use of legume green manures,

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

supplemented with commercial fertilizers, these soils could be built up to a state where they would produce good crops of vegetables, fruits, and forage crops without the use of farm manure. His work on soil organisms and the part they play in the decomposition of organic matter and the improvement of soils was so outstanding that today thousands of farmers throughout New Jersey, and in other states and other lands as well, owe Doctor Lipman a debt of gratitude for this work. Soon there followed his book on "Bacteria in Relation to Country Life," which deals specifically with many of the problems of farm life, such as the care of dairy products, sanitation and sewage disposal, and the production of silage. His work as a Farmers' Institute lecturer under Franklin Dey in the early years of this century gave him an excellent opportunity to meet the farmers of the state; wherever he went he made friends. The fact that he was always in demand as a speaker, having far more calls than he could meet, gave striking evidence of his popularity with the farmers. Likewise as a teacher in the four-year courses and in the short courses at Rutgers he made many friends who gave him loyal support when they went back to the farm.

On the death of his predecessor in the summer of 1911, Doctor Lipman was made director of the Experiment Station. This gave him a wider field of usefulness and a greater opportunity to use his knowledge and experience in the interest of New Jersey farmers. Even before he was made director, he saw the need for a careful survey of the soils of the state. The Bureau of Soils of the U. S. Department of Agriculture had already surveyed, mapped, and published results on the Salem and Trenton areas. About 1910, through the coöperation of the Geological Survey of New Jersey, the Bureau of Soils of the U. S. Department of Agriculture, and the Experiment Station, Doctor Lipman was enabled to make a start on the survey of the Sussex area. A report of this survey was published in 1913. From the beginning of that work until all of the geological areas of the state had been surveyed and mapped, Doctor Lipman did not relinquish his purpose to compile a complete record of the soils of the state. Not only was the survey completed several years ago, but samples of soil representing practically every type in the state have been collected and analyzed, thus giving an inventory of the soil resources of the state.

Early in his administration as director, he saw the need for strengthening and enlarging the staff of workers and adding new departments. This, however, could not be done without increased appropriations, and increased appropriations could not be obtained without convincing legislators that such increases were necessary. Doctor Lipman's thorough knowledge of agricultural conditions in the state and his wide acquaintance with leading farmers and prominent business men enabled him to convince the members of the Legislature that there was a real need for greater support for agriculture in the state. Every year for the last 25 years he has gone before the Legislature with such convincing pleas that he has been able to enlarge the staff of workers

and add buildings and equipment to meet the increasing demands. A man of narrower views, with less knowledge of the problems which awaited solution and with less courage, would long ago have tired of going each year to a busy Legislature to convince its members that agriculture was sorely in need of help. But in this work, as has already been intimated, he had the loyal support of leading farmers, former students, service clubs, county organizations, and many others. But to Doctor Lipman an experiment station that can successfully meet the demands that are made upon it means more than buildings and equipment. He has realized that these material things are of little value without men of sound judgment, thoroughly trained for the work, and possessed with a spirit of real service.

His ability to forecast the trends of agricultural practice has enabled him at all times to be several steps ahead of actual requirements. Soon after his appointment as director, he visualized the possibility of a poultry industry in the state and proved his faith by appointing a poultry husbandman and establishing a department of poultry husbandry. The rapid development of this department and the steady growth of the industry in the state have fully justified his vision. In rapid succession came the departments of plant pathology, of agricultural extension, of vegetable gardening, of dairy husbandry as distinct from animal husbandry, of plant physiology, of agricultural engineering, of seed control, of water supplies and sewage disposal, of ornamental horticulture, and of agricultural economics.

Doctor Lipman's keen knowledge of human nature and his ability to choose the right man for the place and then give him a free hand and the needed equipment for his problem have been a strong factor in his success in advancing New Jersey agriculture. Rarely does one find an administrator who combines such sound organizing ability with a liberal attitude and high standards of achievement. He saw the general problem and then trusted the department head to work out the details, at the same time giving him encouragement and seeing that he had the necessary facilities for carrying on the work. Nor did he overlook the practical side of the problem. When a piece of research was completed he made it possible for the results to be taken to the farmer. This was accomplished through the Extension Service, through lectures by heads of departments, through news releases, farm papers, correspondence, and personal visits by members of the staff.

At times, during the past 25 years, there have been influences tending in the direction of making the Agricultural College a vocational or trade school. When such an issue has been raised, always Doctor Lipman has taken a firm stand in favor of a thorough training in the fundamental sciences. Very largely through his influence the standard has been kept high, and thus the Agricultural College has sent out men of sound training, to take their places on the farm, in research, as county agents, in industry, in agricultural journalism, and in many other fields.

During the War, Doctor Lipman, as director and dean of the Agricultural

College, had many difficult situations to face. A large number of the staff entered the Service, and commercial organizations were competing with the stations for men who had been carefully trained for specific work. Notwithstanding this, Doctor Lipman, with the staff that he was able to hold, so planned and directed the work that the station ably took its part in increasing crop production. In this way the value of its work first became known to many. This new challenge to service brought new responsibilities and a necessity for greater financial support. New demands for service from farmers' organizations scattered here and there over the state brought many new problems. Again Doctor Lipman's vision and foresight enabled him to forestall trouble by asking the coöperation of the leading state farmers' organizations in the planning of some of the important research projects. The State Potato Growers' Association, State Poultry Association, State Horticultural Society, and the American Cranberry Growers' Association each responded by appointing a committee to visit the station and consult with the staff members who were directly concerned with the work of these organizations.

Special appropriations granted in most instances at the request of interested groups, were made for new lines of research. Again credit must be given Doctor Lipman for anticipating a broader service for the station. In the years immediately following the World War, he realized that the rapid urban and suburban development in the state would bring to the station new problems, and was convinced that this new challenge must be met. Thus there was inaugurated research in water supplies and sewage disposal, in agricultural biochemistry, in farm economics, and in landscape gardening; short courses were established in turf management, cheese making, ice cream manufacturing, and ornamental horticulture.

An ancient writer<sup>2</sup> has said, "Where there is no vision, the people perish." Doctor Lipman is a man of vision and having had a vision of what things should be, he has done yeoman service to bring these things to pass. He has seen clearly the changes and developments that are taking place in the agriculture of the state and nation and has thrown his power and influence on the side of constructive improvement. He has consistently advocated the control of soil erosion; he has, in season and out, preached the gospel of soil improvement through the use of lime, fertilizer, and green manures; he has called attention to the necessity for better land utilization, by taking out of cultivation large areas of marginal land, by the creation of additional parks and playgrounds, and by forest conservation; he has ever been watchful of the farmer's interest when laws were being framed to control the manufacture and sale of commercial fertilizer, lime, feeding stuffs, and insecticides, and for the testing of seeds for purity and germination.

A few paragraphs taken from the History of the Experiment Station, published in 1932<sup>3</sup> would seem to form a fitting close for this tribute:

<sup>2</sup> *Proverbs* 29: 18.

<sup>3</sup> Woodward, C., and Waller, I. G. 1932 New Jersey's Agricultural Experiment Station, 1880-1930.

Throughout Dr. Lipman's administration we find the evolution of a philosophy of agriculture leadership—dynamic, but flexible in its relation to public needs....

In his annual report for 1923, Dr. Lipman discussed at length the marked trend toward specialization in New Jersey agriculture, pointing out the problems arising therefrom—insect and disease control, risk from crop failures, and poor markets. The Station, he said, should shape its program with due consideration for these conditions.

Subsequently we find Dr. Lipman constantly pointing to social and economic trends as a guide for future policy. Through the agricultural history of New Jersey like a red thread has run the evidence of economic pressure. Metropolitan expansion has meant changes in the types of agriculture, and city interests have penetrated into the country, introducing new economic and social influences....

Finally, Dr. Lipman has urged that the Station's service should be planned so as to fit best into a comprehensive scheme of state development. Research, he has claimed, must be organized not only to meet present day needs but to provide for far-reaching future adjustments in the agricultural industry.

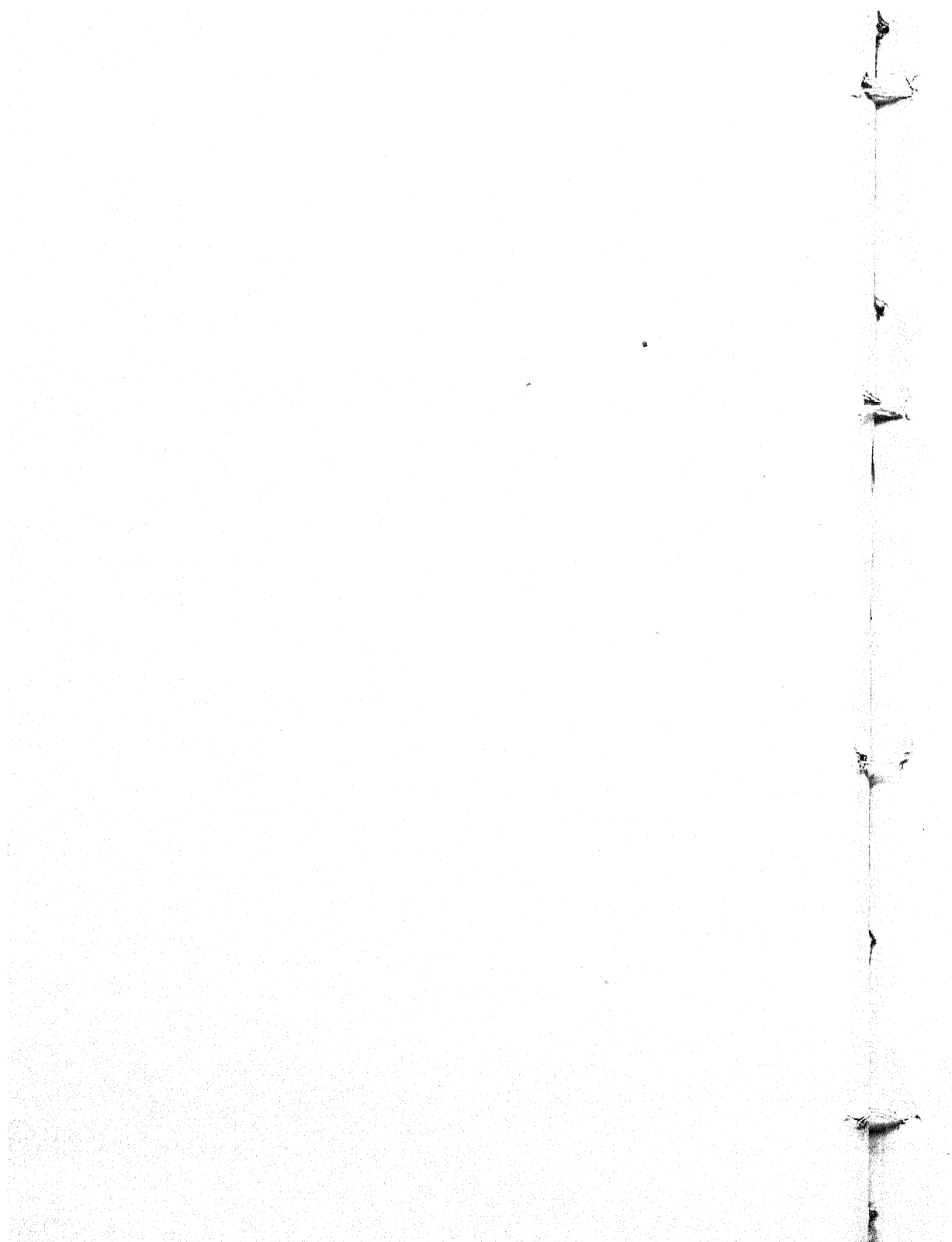
Doctor Lipman himself has expressed his vision of the future services of the station in the following manner:<sup>4</sup>

As the agriculture of the state changes and as the needs of the state as a whole change, adjustments must be made for dealing with the problems as they arise....

As one looks ahead to the future of the institution he is made to realize both its opportunities and its responsibilities. Together with the College of Agriculture, it must further improve its resources as to land, buildings, and equipment. Cognizance must be taken of the growing demand of our industries for research facilities that only a well organized research institution can provide. With the coming years, our experiment stations will need to reckon more and more with conditions that govern the accepting of research grants from industries who are willing to pay for the research service but who, as a part of the economic life of the state, have a right to expect help analogous to that given to the agricultural industry. Beyond that, various organizations, like those of the livestock breeders, dairymen, gardeners, distributors of various commodities, manufacturers of implements, garden clubs and country clubs—will expect the institution to formulate policies, and to help toward their execution, for the sake of promoting the interests not alone of individuals, but of larger or smaller groups that have an interest in economic and social progress. The station, through its research and educational policy, should aim to make the state more attractive to its residents culturally as well as economically. If this assumption is correct, the institution will need to assume a larger responsibility in dealing with the esthetic and cultural needs of the state.

What more could a man wish to have said of him than that he devoted his whole life to making his State a better place to live in—better for the farmer, for the business and the professional man, for the laborer—for all the people?

<sup>4</sup> Woodward, C., and Waller, I. G. 1932 New Jersey's Agricultural Experiment Station, 1880-1930. (Quoted from *Ann. Rpt. N. J. Agr. Exp. Sta.* 1930: 9-10.)





## JACOB G. LIPMAN AS TEACHER AND DIRECTOR OF RESEARCH

ROBERT V. ALLISON

*Bureau of Chemistry and Soils, U. S. Department of Agriculture*

The essential progress of education and of science through the centuries has been centered around the personalities and teachings or the investigations and accomplishments of a comparatively few individuals who have lived and worked quietly and forcefully. In the development of the agricultural sciences through the modern period one of these gifted leaders, Dr. Jacob G. Lipman, plays the dual rôle of teacher and director of research.

In any effort to describe Doctor Lipman's ability in the one field or to evaluate his accomplishments in the other, one promptly finds how difficult it is to separate the two, since his method and influence, so dominantly inspirational, suffuse them both alike, and the teacher becomes at once a director, and the director, a teacher of the highest type.

Among the many personal attributes that contribute to the well-earned reputation and immediate success of Doctor Lipman as a teacher it is doubtful whether any are of more fundamental importance than the exceptional evenness and continuity of his temperament and patience. I am sure I speak for each and every one of his many students, past or present, when I say that on no occasion is he ever found too busy over other matters, whether in the classroom, laboratory, or office, to go into the finest details of a problem in an effort to develop the fullest possible understanding in the mind of the individual. Always there is that enduring willingness to go to the very end of the way in the discussion of any subject with the hope that there will result a thoroughly comprehensive line of thought or of action, whether it pertain to pure theory in the classroom or to a method of procedure in the laboratory.

Associated with this exceptional facility at all times is, of course, that inimitable sense of humor for which he more recently has become well known. This has assisted him not only in smoothing many a rough spot whether by way of lightening a point of discussion or in disarming argument or debate that promised to become unnecessarily heated. It doubtless has also meant much to him, personally, in bearing the heavy load of responsibility he always has carried with such an air of ease throughout these many years.

Although his unlimited tolerance and patience under the most trying circumstances have provided Doctor Lipman with outstanding advantages from the pedagogical standpoint, it is the sheer keenness and drive of his mind in the extemporaneous analysis of a problem, the vastness of the ready store of knowledge he always has at hand, and the thoroughly precise and orderly manner in which he has developed and maintained this mental encyclopaedia

that constitute the more technical background of his ability and finesse, both as a teacher and as a director of research. Little of the past that is important is ever forgotten; into the future is ever ranging a fine and powerful imagination; during the immediate present there is always that smooth joining of current ideas and experiences to those of the past, in preparation for the days to come, with an apperception of extraordinary clearness. It is his so capable handling of a preeminently able mind in this important field that has enabled him progressively to play the important rôle he has in the international development of scientific agriculture.

Without doubt the boyhood experience of Doctor Lipman on a well-developed Colony Farm in New Jersey under the inspiring instruction of an able teacher of agriculture awakened in him a deep love of growing things and a genuine appreciation of the unlimited possibilities of scientific agriculture. There is also little doubt that the winning of a scholarship at the Baron de Hirsch School which brought him in contact with Doctor Voorhees was a most important milestone in his career. The long period of diligent training in soil fertility, and particularly in soil bacteriology, that followed is a substantial manifestation of the strength of that early faith, constituting, as it did, the sound basis upon which he planned his professional career and developed his life work that has meant so much to soil science.

As a result of his appointment to the teaching staff of Rutgers and, subsequently, to the directorship of the Experiment Station and the deanship of the College of Agriculture he established the most intimate connection possible with both graduate and undergraduate students of agriculture in that institution. Thus did the boyhood dreams, worked out in part, at least, on a New Jersey farm, carry Doctor Lipman up from the fields to the classroom and on through the laboratory to leadership in a new and growing science and to a broad leadership among men.

The development of the New Jersey College of Agriculture with its Graduate School to the high place it now holds is a monument to Doctor Lipman's accomplishments in the field of agricultural education. There can be no question as to the highly important rôle this organization has played in the rural development of New Jersey. It has been through the undergraduate student body of the College of Agriculture that he has touched so many of the present and future agricultural leaders not only of New Jersey but of other states as well in a way that has meant so much to agricultural leadership, especially in rural communities. This has been the finest and most important of the several types of "extension" work for which that institution has been responsible.

As a teacher, Doctor Lipman also has exerted a strong human influence over rural life and culture through the contact he has developed and maintained with the "Short Course" students of agriculture who regularly come to the college for limited periods of instruction in the more rudimentary subjects of agriculture during the winter months. Here, indeed, he has found a direct

approach to the farm and an excellent opportunity to send forth the findings on the experimental plots or in the laboratory to trial under intensely practical conditions by a messenger who will himself eventually be the practitioner and who usually serves also as a demonstrator in his own community. The Short Course in New Jersey has been strongly developed and has come to represent an important instructional unit for those boys who feel they can not afford the time or money to take the regular four-year training. As an assistant to Doctor Lipman in his soil fertility course for these students during several winters, I could not but observe the remarkable opportunity he had thereby developed for a direct contact with those young farmers of the state.

It is also as a teacher, of agriculture, essentially, that Doctor Lipman has played such an important part in the development of New Jersey's remarkably fine extension system to serve what has come to be a highly specialized type of agriculture in most parts of the state. Although extension work in New Jersey began with the passage of the act in 1864 which designated the Rutgers Scientific School the Land Grant College for New Jersey, the elaborate form to which it is now developed is of comparatively recent origin, having followed, naturally, the expansion and elaboration of the experimental phases of the work. Thus, throughout the state, hundreds of farmer's meetings and conferences of one type or another have been organized to follow up those early lectures of Doctor Cook, and later of Doctor Voorhees, on a wide variety of agricultural subjects. At the more important of such public meetings Doctor Lipman has lectured scores of times in practically every part of the state. This phase of the work of the institution has been of the utmost importance in furthering agricultural development since, just as in the instance of the Short Course students, it is the most direct and satisfactory way of converting theory into practice. After all, it has been the applied phase of our research work that has made for the rapid development of American agriculture, even though we may now realize that this development has not always been judicious and sound from every standpoint at all times.

It was likewise as a teacher, in part at least, that Doctor Lipman, shortly after his advancement to the directorship of the Experiment Station, became interested in the development of the Graduate School in the College. Here, however, he also appears in the rôle of director of research, and it becomes more difficult in this, perhaps, than in any other field sharply to differentiate the two functions and to say where the responsibilities of the teacher and those of the director begin and end.

The Graduate School had a most interesting beginning, based largely on the lively interest of important commercial houses in establishing fellowships for the investigation of definite agricultural problems. This was at the time when the importance of agricultural research was coming to be felt very strongly and its control over the production of commodities destined for agricultural consumption was exerting itself rather sharply. Since those early years, 1907-1915, the names of Brown, Lint, Coleman, Koch, Cook, Kopeloff,

and others have impressed themselves on those who have followed, as real pioneers in the early organization of the work and of the school.

It is a further tribute to Doctor Lipman, both as a teacher and as a director, that the quality of the research work developed through those early periods and through its transition into the modern stage was always at par. At all times his students have been inspired by the knowledge that he was making every effort to provide their essential needs in the work. Not infrequently, too, much-needed conveniences have become available at the expense of his personal exchequer. One of the finest of such instances is his personal contribution to the endowment of the Cook-Voorhees Foundation in Soil Science in honor of the earlier directors of the Experiment Station who immediately preceded him. The earnings of the handsome fund that was developed in this cause are now used for the regular support of a research fellowship.

Although the early work of the Graduate School centered largely in soil fertility and closely allied subjects it broadened rapidly as the institution grew, until it now involves practically all the fields covered by the work of the College and of the Experiment Station. It would be invidious, indeed, to single out the work of particular departments for mention in a space so small as to preclude reference to the programs and progress of all. Suffice it to say that the researches and findings in many, if not all of them, have been distinctly basic to the science they represent and, as such, have attracted wide attention. Among them, the Department of Soil Chemistry and Bacteriology, always closest, of course, to the heart of Doctor Lipman, has doubtless led the way to the international recognition which the institution now enjoys.

In his rôle as teacher in the development of the Graduate School, Doctor Lipman's contacts became much wider than the confines of the state or even of the nation. As early as the mid-period of its development, 1915-1920, his name in the field of soil science had become internationally known, and students from many foreign countries began to find their way to Rutgers. This was largely through his numerous scientific writings and SOIL SCIENCE, which he established, as well as his frequent attendance upon, and important contributions to the success of, scientific meetings abroad. At the present time this institution can probably claim a more cosmopolitan alumni group than any other Graduate School of its size in the country. Included in the list of foreign countries from which students have come to New Brunswick to study under Doctor Lipman are: Australia, Austria, Belgium, Brazil, Canada, China, Cuba, Czechoslovakia, Denmark, England, Estonia, France, Germany, Greece, Holland, India, Japan, Palestine, Puerto Rico, Russia, Santo Domingo, South Africa, Sweden, and Switzerland. This group has included fellowship holders from the International Education Board, from the Scandanavian-American Foundation, and from numerous other organizations and has joined students from time to time with various expeditions as soil scientists or representatives of other branches of agricultural research from this organization. Thus the development of the Graduate School at Rutgers has been one of the

really important sources of recognition for Doctor Lipman in soil science and has been used by him, in turn, as an effective instrument in the part he has played in the development of that science.

As a director of research, naturally Doctor Lipman's most important work has been in the development of the Experiment Station. In order to appreciate fully the great task he inherited from his predecessors in the work, one must visualize, briefly at least, the development of New Jersey agriculture from Colonial times.

First of all there was, of course, the gradual decline of agricultural production through the post-revolutionary period due to exhausted soils and to the absence of much-needed information on proper fertilizers and cultural methods. This extended well past the beginning of the nineteenth century, when the situation was periodically depressed or relieved by such circumstances as the Embargo Act, the War of 1812, and depressions, all of which led up to the so-called "Industrial Revolution" following 1830 that marked the transfer of the manufacture of clothing and of implements from the household to the factory. By 1850 the factory movement was well under way, and "commercialized agriculture" came into being with its rapid development of specialized implements for various operations and the use of marl, chemical fertilizers, and clovers, which had become an established necessity based on fact.

Between 1850 and 1860 there was a continued rapid and irrepressible development in agriculture. This was capped by the high war prices of 1861-1864. The post-war depression marked a turning point in the development of New Jersey agriculture, however, due to the early appearance of western competition in general farm products against those available from the high-priced land near the rapidly developing metropolitan areas of the East. This was the point where the New Jersey farmers turned to specialties in the form of vegetables, fruits, meat, and poultry. The "Experimental Farm" or "College Farm" was established in 1864 following the passage of the Morrill Land Grant Act in 1862 and the designation of Rutgers as the State College for the Benefit of Agriculture and of Mechanic Arts in 1864. There followed a varied program at the farm, involving many practical and important studies that continued up to 1880, when the Agricultural Experiment Station was formally established.

In the early work of the station it was quickly observed by Doctor Cook that "questions of soil fertility were most important both in scope and in the usefulness of results. . . ." During this period were also inaugurated a great variety of crop trials that contributed greatly to the later program of expansion under Doctor Voorhees. In this latter period the program of research was greatly enlarged, and broad efforts were made at a systematic extension of the results to the farmers of the state just as rapidly as possible—the forerunner of the present, comprehensive Extension Service. So we find the Experiment Station at the time Doctor Lipman took charge of it in 1911 fully ready for the period of specialization and readjustment that rapidly followed both in the fields of research as pertaining to the individual workers

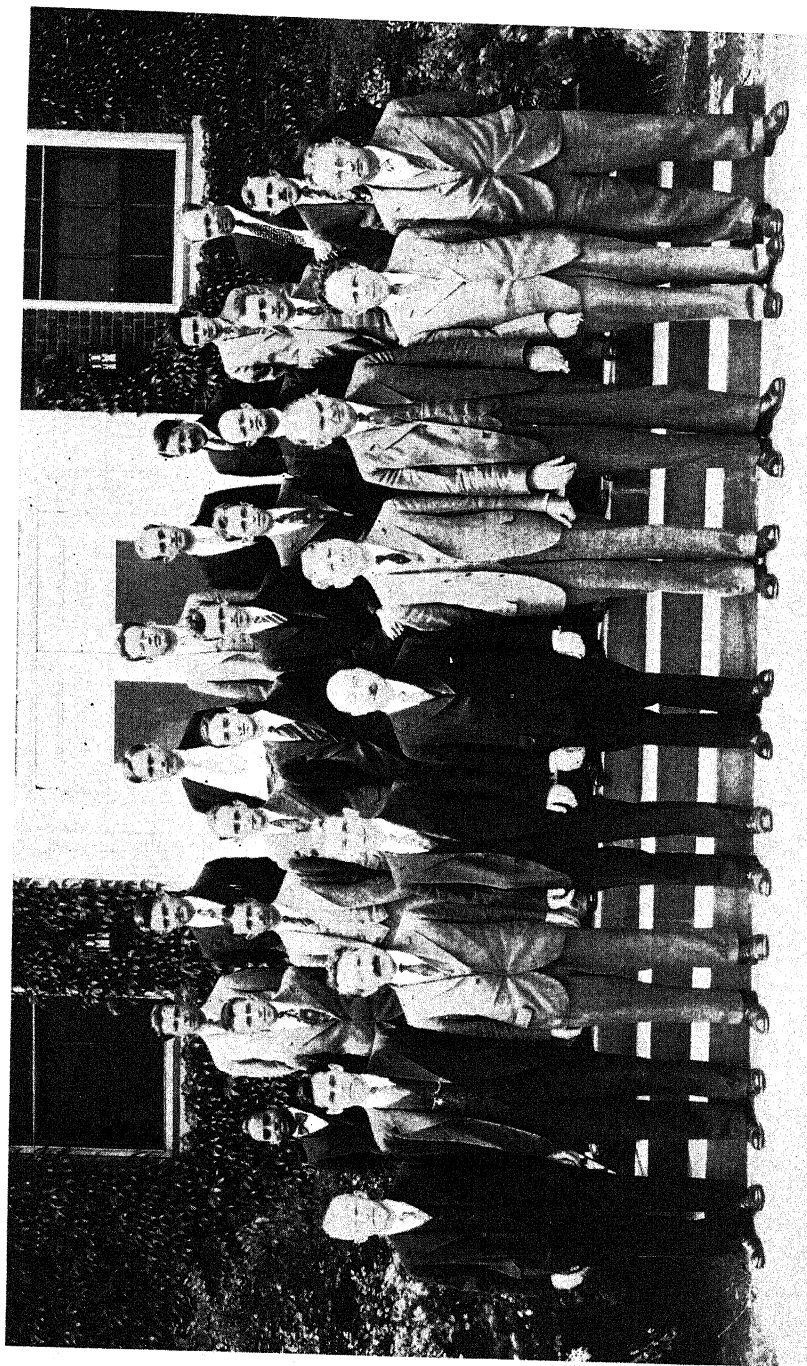
and to the departments of work and in the agricultural enterprise which that research was to serve.

Although chemistry in its relation to soil fertility and to the composition of feeds was the dominant branch of the work in the early period, even prior to the establishment of the Experiment Station when basic studies in plant requirements were under way at the "College Farm" [marl and other studies (1868); fertilizer trials with wheat (1869), with cabbage (1870), with corn (1872); etc.], this was destined to give way to the Department of Soil Chemistry and Bacteriology and itself become largely a control division in the organization entrusted with the important work of fertilizer and feed control analyses.

At the time Doctor Lipman became director, the work of the Experiment Station was centered largely around five divisions of investigation established during the years indicated: biology (1888); entomology (1888); botany (1889); horticulture (1895); and soil science (1898). With the sharp trend toward specialization and the demands imposed by the World War for ever higher agricultural production, the organization of new departments of work in the Experiment Station progressed rapidly under Doctor Lipman's leadership. Up to the present time, twelve new but closely harmonized sections have been added. These include: plant pathology (1911); poultry husbandry (1911); seed analysis (1912); dairy husbandry (1912); extension service (1912, though informally inaugurated 1864); agronomy (1914); agricultural economics (1917); plant physiology (1918); agricultural engineering (1918); agricultural biochemistry (1925); and water and sewage research (1927). There are, too, the important departments of publications and library, which have grown steadily into an important part of the organization as a whole.

Thus it has been the ever quick and full recognition of the changing trends in agricultural development and the rapid fashioning of the investigational program to fit its varying needs that have made the Experiment Station such an important factor in the establishment of this most essential of all industries upon a thoroughly sound basis throughout the East. Frequently, however, it has not followed changes in agriculture but rather, through its pioneering studies, has anticipated the definite needs of the future and so has contributed in a very definite way to the deliberate moulding of the agricultural destiny of the State of New Jersey and of the Nation.

Although Doctor Lipman's work as a scientist has been in the field of soil fertility and especially in that of soil microbiology, the breadth of his understanding and the range of his vision in the development of American agriculture, whether as a teacher or as a director of research, are best exemplified in the fine institutions in the founding of which he has played so prominent a part. Since the establishment and perpetuity of this work have been so close to his heart for so many years, perhaps in closing these remarks upon his career as a teacher and director, we can best say with Sir John Russell, "Our sincere wish is that it [the Experiment Station] may long continue its prosperous career and that it may be as successful in the future as in the past in maintaining a great reputation through the excellence of its work and the distinction of its staff."



MEMBERS OF THE DEPARTMENT OF SOIL CHEMISTRY AND BACTERIOLOGY OF THE NEW JERSEY AGRICULTURAL EXPERIMENT STATION, 1932





## EARLY FERTILIZER WORK IN THE UNITED STATES

OSWALD SCHREINER

*Division Soil Fertility Investigations, U. S. Department of Agriculture*

### EARLIEST INTEREST IN FERTILIZERS

Perhaps the earliest definitely experimental work on soil fertility is that done in 1760 by George Washington, who was deeply interested in the conservation and improvement of soils. In the absence of commercial fertilizers he made many experiments with manures, marl, gypsum, and a variety of green manures, including lucerne (alfalfa). He also experimented with the use of common salt, dividing the field into 8-foot treated and untreated strips.

J. A. Binns of Loudoun County, Virginia, also began experimenting with gypsum in 1784 and after 19 years of experimental work published his results in a book, "A Treatise on Practical Husbandry," in which he described tests with various cereals and forage crops. Another early record on the use of gypsum states that about 1770 Jacob Burge used it in a garden in Philadelphia, Pa., which was observed by Richard Peters, afterward president of the Philadelphia Agricultural Society. Peters then extended these experiments with commercial gypsum on his own farm, which was located in what is now Fairmount Park.

C. T. Jackson describes, in the 1844 Report of the Commissioner of Patents, a commercial fertilizer based on the analysis of Peruvian guano. In this he used such substances as phosphate of lime and soda, carbonate and muriate of ammonia, sulfate and nitrate of potash, nitrate of soda, sulfate of magnesia, oxides of iron and manganese, and organic ammoniates derived from peat. This appears to be the earliest attempt at the preparation of artificial fertilizer mixtures in America. It is especially interesting to note that he included sulfate of magnesia and also compounds of manganese; the inclusion of these substances in fertilizers today is considered a new and developing problem.

It would appear that the first Act in the interest of agriculture was passed by the Legislature of Maryland in 1847, establishing the office of agricultural chemist to analyze soils, marls, and vegetable and mineral deposits of practical utility to agriculture. Dr. James Higgins in his three annual reports as incumbent of that office reports on the analysis of soils and fertilizer materials, but whether he made any field experiments is doubtful. He reports some field experiments by coöperating farmers. In his third report (1853) he says:

I am happy to inform your Honorable Body that all and more than all which can be accomplished by an experimental farm, at the public expense, I have made arrangements to accomplish, by the aid of several public spirited gentlemen of our state. . . . have each agreed to set aside a portion of their farms for a series of carefully conducted experiments with differ-

ent manures on different crops . . . they will form the first and only experiments yet made in our state or elsewhere, where all the causes influencing the production of a crop will be estimated and the separate value assigned to each.

These early investigators were strongly influenced by Liebig, in Germany, and by Lawes and Gilbert, in England. Higgins pays his respects to the former as follows:

Baron Liebig—a master genius—one of those great, vast and comprehensive minds, whose ideas become facts for mankind—reviewing the experience of those who had preceded him, and exploring with indomitable energy and skill the composition of the earth—giving to each tree, plant and shrub a tongue to utter words of eternal truth—to disclose their composition, and to show their necessities, has explained the laws for the production of vegetable life, in a simple and plain, yet thorough and irrefutable manner.

After discussing some of the results of Lawes and Gilbert he writes these words of appreciation:

The whole agricultural community, both in this country, as well as in England, are under deep obligations to these gentlemen, who, through a long series of years, conducted such careful and accurate experiments. These papers, and others which have preceded it, have given me and the people of our State much valuable information. I hope this will be some slight reward for their laborious experiments.

#### ESTABLISHMENT OF FIELD TESTS AND CONTROL LAWS

In 1856 the Maryland Legislature passed an Act to establish an agricultural college, and in 1858 field experiments to test the relative values of the different manures (fertilizers) offered for sale in Baltimore and Washington were commenced on the college farm but were interrupted by financial distress and political unrest in state and nation.

Levi Stockbridge, of Massachusetts, in 1867 began experiments with commercial fertilizers on the college farm and inaugurated pot experiments with the thought that the nutritional needs of the plant are determined by the chemical composition of the plant. He extended this experimentation to large boxes in 1871 and in 1875 concluded that the only substances the farmer must supply were nitrogen, potash, and phosphoric acid, and that there was a relation between crop and quantity of fertilizer applied, if these elements were supplied in the proportion found in the *entire* plant. He devised fertilizer formulas for many crops and in 1878 contributed the royalties derived therefrom for the establishment of an experiment station, which in 1882 became the Massachusetts Agricultural Experiment Station by Act of the State Legislature. F. H. Storer, dean of the Bussey Institution, Massachusetts, in 1871 inaugurated field tests of fertilizers on the farm of the Bussey Institution and made analyses of commercial fertilizers.

The report by C. A. Goessmann on commercial fertilizer analyses in 1873 led to the enactment of the Massachusetts Fertilizer Control Act of May 26, 1873, the first law in the United States providing for an official inspection of fertilizers. He was among the first to study the effect of different fertilizers on

the composition of fruits and showed that the relative proportions of the fertilizer elements affected the quality of the fruits.

In 1853 William Johnson, at Yale Scientific School, Connecticut, published an article on superphosphate of lime in the *Country Gentleman* of February 1853, discussing the value of commercial fertilizers. In the same journal a year later, writing from Munich, Germany, in discussing the Moeckern Agricultural Experiment Station, he extolls "the great utility of such establishments and the hope that the organization of similar ones in the United States may be encouraged." On his return in 1855 he resumed his work of analysis and valuation of fertilizers and continued to agitate the question of fertilizer control. His work in keeping inferior or worthless fertilizers off the market in Connecticut, aroused public interest throughout the next two decades and resulted in the establishment of a State Experiment Station at Middletown, Connecticut, by Act of Legislature, with W. O. Atwater as director. Analysis of fertilizers was inaugurated, and farmers were urged to submit samples. In 1876, probably the first joint meeting of farmers and fertilizer manufacturers and dealers in the United States was held under the auspices of the station. This meeting recommended that all fertilizers sold in the state should be sold under a guarantee of composition to be determined by the station. Box and field experiments were conducted with W. H. Jordan as associate. In 1877 the station was removed to New Haven with Samuel W. Johnson as director. This important agricultural research and the valuation of commercial fertilizers on a scientific basis was pioneer work, and its influence extended widely throughout the United States.

In 1855 McAllister, near the general site of what is now the Pennsylvania Experiment Station Farm, supervised the laying out of experimental tracts on the school farm and planned experiments in the rotation of crops and the application and use of fertilizers. This Farmers' High School became in 1862 the Agricultural College of Pennsylvania, and in the first ten years of its existence its efforts were confined to simple experiments with fertilizers and methods of culture.

The first lysimeter work in America appears to be that done between 1867 and 1875 by E. L. Sturtevant, who later became the first director of the newly established New York Experiment Station. This lysimeter work was done on a farm owned jointly by him and his brothers near South Framingham, Massachusetts, known widely as Waushakum Farm, and was used in connection with studies on the percolation of water in soils and drainage experiments.

Although Maine, in 1868, began some simple fertilizer experiments, it was not until 1880 that an experiment testing the different forms of phosphoric acid was started; this was later extended to include various fertilizer combinations.

While manager of the college farm in Ohio, Charles E. Thorne, under the early direction of Prof. N. S. Townshend, started some fertilizer and culture

experiments with several crops during the period of 1877 to 1881. In Tennessee some early work with fertilizers on wheat and pasture was started by J. M. McBryde. The results of some fertilizer work on cotton done by the college on a tract of land in northern Alabama were published in 1875; and later fertilizer work was done at the college farm with cotton, corn, and potatoes. In Wisconsin, there were some early experiments between 1875 and 1880 by W. W. Daniells with fertilizer on corn. In Louisiana, W. C. Stubbs conducted some early experiments with fertilizers on sugar cane, oats, and corn at the Sugar Experiment Station established in 1885, and later with cotton, oats, and potatoes, at the State Experiment Station.

On the Experimental Farm of Illinois Industrial University, W. C. Flaggs started some fertilizer experiments in 1871, and in 1872 Kansas began some experiments with fertilizer; Cornell University Experiment Station published in 1880 its first report on fertilizer experiments begun in 1878; in Kentucky, M. A. Scovell reported in 1885 on a fertilizer experiment with tobacco and later with other field crops; in Indiana, from 1879 to 1882 there were some fertilizer experiments with wheat, corn, oats, and grass, reported by C. L. Ingersoll; in Mississippi, F. A. Gulley conducted some fertilizer experiments with cotton and corn during the period 1880 to 1888; in Missouri, J. W. Sanborn reported fertilizer experiments on corn and wheat during the period 1883 to 1888; and in New Hampshire, G. H. Whitcher, conducted experiments with fertilizers before 1888.

At Pennsylvania State College, W. H. Jordan conducted, from 1881 to 1885, some general fertilizer experiments with dissolved bone black, ground bone, nitrate of soda, dried blood, sulfate of ammonia, muriate of potash, lime, ground limestone, plaster, and yard manure; experiments to show the effects of different forms of phosphoric acid on crops in rotation; and experiments with wheat using different amounts of commercial fertilizer.

Through the influence of G. H. Cook, professor of chemistry at Rutgers College, New Jersey, field experiments with fertilizers were begun in 1865. It was not until 1874, however, that an Act for the control of fertilizers was passed and control work undertaken by the institution. The New Jersey Agricultural Experiment Station was not established until 1880, when it took over the control and experimental functions of the college, with Professor Cook as director. The station followed the lead of Johnson at the Connecticut Agricultural Experiment Station in its conduct of fertilizer control work. Field Experiments with fertilizers were carried on at the college farm and also coöperatively with farmers in various parts of the state with different crops, and with analyses of these to determine the amounts of plant foods removed per acre. This early attempt at obtaining an inventory of fertility factors has in later years been extended by the present director, Dr. J. G. Lipman, in an excellent manner to the national domain.

The North Carolina Agricultural Experiment Station was established in 1877 and was authorized to analyze fertilizers, suppress fraud in the sale of com-

mercial fertilizers, and carry on experiments on the nutrition and growth of plants. Its right to publish analyses was challenged, and the question of the constitutionality of the fertilizer law was taken to the State Supreme Court, which decided in favor of the Department of Agriculture, thus settling an important question in fertilizer control administration in other states.

These early stations in Connecticut, Massachusetts, New Jersey, and North Carolina began the inspection of fertilizers. This work was strongly supported by the farmers and served an excellent purpose in improving the quality of fertilizers, and, by restraining the fraudulent, the control movement was of great help to the more honestly inclined fertilizer producers. The enactment of laws for fertilizer control soon spread into about 20 states east of the Mississippi River, where, under the influence of the Association of Official Agricultural Chemists, control became thoroughly organized. Although this association was formally organized in 1884, it was the outgrowth of an older Association of Agricultural Chemists formed in 1880, meeting first in Washington, later in Boston, Cincinnati, and Atlanta, and counting among its members such distinguished agricultural chemists as Goessmann, Johnson, Wiley, Jenkins, Caldwell, and Atwater. With the merging of this earlier association into the Association of Official Agricultural Chemists, S. W. Johnson became its first president, and H. W. Wiley, its second president in 1886. The latter as founder and secretary-treasurer from 1890 to 1912 became its militant leader for honesty and purity in foods, feeding stuffs, and fertilizers, with guaranteed analysis for the latter and chemical control by state chemists.

#### EXPERIMENTAL WORK SUBSEQUENT TO THE HATCH ACT

After the passage of the Hatch Act in 1887 the scientific work of the experiment stations was greatly extended, and fertilizer work shared in this general improvement. Such fertilizer experimentation was rather largely confined to the older states east of the Mississippi River. The following will illustrate in a general way the character and scope of this period of fertilizer investigation by some of the state stations:

The Connecticut Station conducted studies on the effect of fertilizers on the chemical composition of corn, and various nitrogen sources were studied as to availability on different soils; the Massachusetts Station studied the effects of special fertilizers on fruits, vegetables, and field crops, investigated the effect of different plant food combinations on quantity and quality of tobacco grown in the Connecticut River Valley, and experimented on the relative value of different phosphates and potash carriers; the New Jersey Station made cylinder experiments on the relative availability of nitrogenous fertilizers and barnyard manure and conducted field experiments with various fertilizer materials and combinations; the Ohio Station made a long continued investigation relating to the maintenance of soil fertility which comprised experiments with fertilizers and manures on hundreds of tenth-acre plots on various

soil types of the state; the Illinois Station continued its field work on the management of soils in many regions of the state and made pot experiments with the different soil types of the state; the Kentucky Station by field experiments showed that the depleted bluegrass soils of the state were deficient in potash and conducted fertilizer experiments with tobacco, hemp, and corn, studying the effect of fertilizers on shrinkage and on the ratio of cob to kernel; West Virginia made 5-year comparisons of commercial fertilizers with barnyard manure in pasture studies; Mississippi studied the effect of fertilizers on cotton on a variety of soil types of the state; Louisiana similarly studied the effect on sugar cane over a long period of years; the Alabama Station determined the fertilizer needs of its important soil regions and particularly studied green manuring; North Carolina studied the use of tobacco by-products, the effect of commercial fertilizers on the various important soil types of the state, and the effect of different fertilization on nitrification in the soils and the availability of phosphates as affected by fineness; South Carolina studied the ratios of nitrogen, phosphoric acid, and potash for best cotton and other crop production and studied different methods of fertilizer placement to obtain maximum results.

#### LONG TERM FERTILIZER EXPERIMENTS

Special mention should perhaps be made here to our long term experiments in the United States, which were inaugurated in these earlier periods of fertilizer experimentation at the Illinois, Pennsylvania, and Ohio Experiment Stations.

The Morrow plots at the Illinois Experiment Station, begun in 1879 by George E. Morrow, are the oldest soil experimental plots in America. The series originally contained seven plots, on part of which use was made of fertilizers and manure. Three of the original plots still remain, the others have been used for building purposes in the development of the University of Illinois. Subsequently other experimental plot work was begun in 1902 on the North Farm and in 1903 on the South Farm of the Experiment Station, by Cyril G. Hopkins, which are still under observation.

The oldest most extensive plot tests of fertilizers are those by the Pennsylvania Agricultural Experiment Station laid out in 1881 by W. H. Jordan. Four tiers of 36 plots, each one-eighth acre, are used for the growing of corn, oats, wheat, and mixed clover and timothy in rotation on Hagerstown clay loam, a prominent soil of the region. The objects were to test the comparative effects of the following treatments on the crops grown: single fertilizer ingredients; combinations of two ingredients; complete fertilizers; nitrogen in different forms and amounts; superphosphate and ground bone; manure in different amounts in comparison with commercial fertilizers; burnt lime and ground limestone used alone, and burnt lime used with manure; and land plaster. Jordan applied nitrogen, phosphoric acid, and potash at the rates of 24, 48, and 100 pounds, respectively, per acre as the standard treatment every second year, and on the corn and wheat crop different rates of nitrogen; namely, 24, 48, and 72 pounds per acre were applied in alternate years, using three different forms of nitrogen—dried blood, sodium nitrate, and ammonium sulfate.

The investigational plot work on fertilizers was begun at the Ohio Agricultural Experiment Station in 1893 by Charles E. Thorne, growing corn, oats, wheat, clover, and timothy in rotation, with applications of nitrogen, phosphoric acid, and potash, singly and in combination. With these tests at Wooster and at a number of other points in the state, Ohio has probably the most extensive outlay of plots in the United States.

In this connection the long term cylinder experiments of the New Jersey Experiment Station begun in 1898 and continued to this day by Dr. J. G. Lipman and Prof. A. W. Blair should also be mentioned. Corn, oats, wheat, and timothy were grown in rotation in 60 cylinders, each 4 feet deep and  $23\frac{1}{2}$  inches in diameter, open at both ends and set into the soil to simulate natural drainage as much as possible. Since the availability of nitrogen from different sources was the main object of the experiments, manures, dried blood, sodium nitrate, and ammonium sulfate were used in various combinations.

After the passage of the Adams Act in 1906, granting government support to research at the state experiment stations, another period of development in soil science began. There were studies of the fertilizer requirements of the principal soil types in different states; of the composition of certain plants as indicative of these requirements; of the effects of fertilizers on quality of crops; of the rôle of fertilizer constituents in plant nutrition; of the functions of lime; of the so-called deficiency diseases; and of many other lines of fertilizer research, thus bringing us up to the more recent developments which, however, lie outside of the scope of this brief summary of the earlier work in fertilizer experimentation in the United States. There remains to sketch even more briefly the development of the early fertilizer industry in the United States.

#### EARLY DEVELOPMENT OF THE FERTILIZER INDUSTRY

The use, production, and sale of commercial fertilizer seem to have had their origin in Maryland. According to the Report on Agriculture of the U. S. Commissioner of Patents, 1854, guano was first used about 1824, when the editor of *The American Farmer* received two barrels of guano at Baltimore and distributed it for experimental purposes. P. T. Tyson in his first report as state agricultural chemist for Maryland, published in 1860, states that, "Maryland was the pioneer State in the use of guano in this country. According to my recollection, the first trial of it in the State was by Capt. A. S. Dungan, of a few bags brought by him from Peru, and applied to part of his corn crop. This I think was about the year 1832, and soon after the importation of it by the cargo was commenced." Baltimore City was the first and for a long time the only port for the importation of guanos from Peru, the Caribbean Sea, and the Gulf of Mexico. Some twenty barrels were shipped here from England, in 1840, but the first direct shipment from the Chincha Islands of Peru was received in 1841. For some time the guanos were used in their crude state, but soon became "manipulated." Guano reached its maximum importation into the United States in 1856, when it amounted to 50,000 tons. This entire

amount passed through the Baltimore market, and at that time no fertilizers were sold west of Pennsylvania. Likewise, Tyson in 1860 states, "The first bones used for manure in this country, it is believed, were crushed at the establishment of Mr. Wm. Trego, and sold to farmers in Harford and Montgomery counties in the year 1836."

In the third report by James Higgins, first agricultural chemist of the State of Maryland, published in 1853, there are enumerated and classified a considerable number of fertilizer materials then occurring in commerce, among them, guano, poudrette, bonedust, pure lime, magnesium lime, mineral phosphate of lime, wood ashes, potash, nitrate of potash, nitrate of soda, gypsum, shell marl, and green sand marl (Jersey marl). These appear to have been in use in 1853, but the specific dates of introduction of some of them are not so clear. In 1860, P. T. Tyson, second agricultural chemist for Maryland, devotes a chapter in his report to "Artificial Manures of Fertilizers," discussing the uncertain composition and money value of many of these, and giving suggestions "for protecting our farmers from frauds in fertilizers and adulterated guanos and other manures." The "brand" idea was already well developed, for he mentions such names as "Mapes' Super-phosphate," "Mapes' Nitrogenized," "DeBurg's Super-phosphate," "Coe's Super-phosphate," and others. Dr. R. W. L. Rasin—descended from an old Maryland family, and engaged with the Philadelphia Guano Company when it was organized in 1854 to work the guano producing islands near the coast of Venezuela, remaining with them until these were exhausted—states that in 1850, Chappell and Davison of Baltimore made some fertilizer in a small way at the same time that Mapes was experimenting. DeBurg made use of spent bone black from the sugar refineries, calling his product "dissolved bone black." Manufacture on a commercial scale was begun about 1853 by Mapes and by Rhodes, both in Baltimore. In 1855 Kettlewell, claiming to produce a more suitable agricultural product, produced his so-called "Kettlewell's manipulated guano," which appears to have been a mixture of highly nitrogenous Peruvian guano with highly phosphatic Mexican guano.

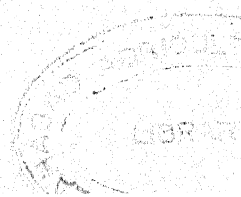
C. T. Jackson, of Boston, Mass., writes in the 1854 Report of the Commissioner of Patents (Agriculture) that a company had been formed in Rhode Island "for the manufacture of fish manure, and the fat menhaden of Providence river and Long Island sound will be used to produce both oil and fish-cake, and the latter being duly prepared so as to render it inodorous, will be sent into the agricultural market as an artificial guano." He also refers to acidulating the fish-cake. Although fish has been used since earliest times, even by our American Indians, this appears to be the first commercial manufacture of fish guano.

Sir John Lawes about 1842 invented the process of making superphosphate from natural rock phosphate with sulfuric acid in England, following the same idea suggested by Liebig for the sulfuric acid treatment of bone in 1840. This process soon came to be used in the United States. Baltimore became the first



center for the production of chemical fertilizers in the United States about 1850; this commercial production later extended to Richmond, Va., and Charleston, S. C. The quantity produced and sold was at first small, but in the next six years the use increased to 20,000 tons in the United States. The number of manufacturers was small, but by 1860 the census reports as many as 47 firms engaged in the manufacture of artificial or commercial fertilizers. With the development of the South Carolina phosphate beds in 1868 the industry was given a new impetus. Charleston soon became an important superphosphate manufacturing center, seven companies being engaged in the industry in South Carolina in 1870. The even more extensive deposits in Florida were not yet discovered and were not a commercial factor until 1888. The Tennessee deposits did not become commercially important until after 1892.

The industry grew rapidly from its small beginnings in 1850 to about 20,000 tons in 1856, and census figures show that by 1869 the production of fertilizers in the United States was about 153,000 tons, by 1889 about 1,900,000 tons, by 1909 about 5,600,000 tons, and by 1927 about 8,000,000 tons. From the pioneer days of the fertilizer industry a remarkable evolution in fertilizer manufacture has taken place, and the industry is now primarily a chemical one, dependent to a considerable extent on relatively pure chemical compounds.





## THE BEGINNINGS AND DEVELOPMENT OF SOIL MICROBIOLOGY IN THE UNITED STATES<sup>1</sup>

P. E. BROWN

*Iowa State College*

Soil microbiology, or "soil bacteriology," as it was known for many years and is still called in some quarters, probably largely for sentimental reasons, is one of that great progeny of modern sciences developed during the latter part of the nineteenth century, the so-called "Golden Age of Science," from that prolific mother of so many sciences—Agriculture. It appeared along with Bacteriology, itself a child of Botany, one of the newer biological-agricultural sciences. And it also grew up along with soil science or pedology, another of the newer agricultural sciences, which developed largely from agricultural chemistry and geology. From these two closely related fields it derived its early name—"soil bacteriology"—and from both it drew techniques and viewpoints. But it also borrowed methods and theories from chemistry, physics, and other older sciences. In fact, as a science, soil bacteriology overlaps so many other fields that there has been some confusion as to its proper place in the whole scheme of science. But in this characteristic, it should be emphasized that it is no different from most of the modern so-called "applied sciences." And the complex relationships of the science should raise no question of its status as a distinct branch of knowledge. By all the criteria which are generally agreed upon as adequate, soil microbiology is certainly approaching maturity as a science, if, indeed, it is not quite full-grown now.

Although many suggestions appear in the writings of the early agricultural investigators, indicating the significance of "germs" in relation to crop production, it was not until the eighties of the last century that actual evidence of the occurrence and action of microorganisms in the soil was obtained. Bous-singault in 1858 asserted that the soil contained germs, Pasteur in 1862 claimed that nitrification was a process brought about by a living ferment, Schönbein in 1868 stated that nitrates may be reduced to nitrites by fungi, and Schloesing and Müntz in 1877 proved Pasteur's contention, but it was not until Koch in 1881 developed the gelatine plate method for the isolation of pure cultures that bacteriological studies really began and attempts were made to investigate the microorganisms in the soil.

During the two decades following Koch's epoch-making contributions, many scientists were attracted to this new and important field, and considerable research was conducted to determine the character and significance of the

<sup>1</sup>Journal Paper No. J226 of the Iowa Agricultural Experiment Station, Ames, Iowa.

activities of microorganisms in the soil under varying conditions. Probably no other science developed quite so rapidly, but, be that as it may, the growth of soil microbiology during this period was amazing, and great strides had been made toward its maturity as a science, when investigations began in this country.

Already Hellriegel and Wilfarth had conducted their classical experiments on the fixation of nitrogen by inoculated legumes and effectively settled the controversy which had been raging for many years over the question of the nitrogen nutrition of plants. Already Frank had described the causative organism and named it, and Beijerinck had also isolated the bacteria and given them a different name, thus creating a difficulty in nomenclature which persisted for many years and was not entirely settled even by the official action of the Society of American Bacteriologists. Already Winogradsky had succeeded in isolating the nitrifying bacteria and shown something of the nature of the process of nitrification, accomplishing what many others had attempted but failed to perform because of difficulties in technique. Already this same investigator had isolated and described a free-living anaerobic nitrogen-fixer, *Clostridium pasteurianum*; Berthelot had reported on the gains in nitrogen in fallow soils, presumably due to microorganisms, and a commercial culture, "Alinit," had appeared on the market for use in inoculating soils with nitrogen-fixing bacteria. Already Marchal had demonstrated the production of ammonia by many species of soil bacteria, and Omelianskii had shown the importance of bacteria in decomposing cellulose and had isolated two anaerobes functioning in the process. Already Gayon and Dupetit had isolated two organisms capable of reducing nitrates, Beijerinck had found an organism which reduced sulfates, and Winogradsky had studied the sulfur-oxidizing bacteria. And throughout the period many were studying the numbers of microorganisms in the soil and discussing their importance from the standpoint of soil fertility or productivity.

As it is difficult to fix definitely the time of the beginning of the science of soil microbiology, so is it quite impossible to give an actual date for the beginnings of the science in this country. Certain suggestions and comments regarding the bacteria in soils and especially regarding the growth and value of inoculated legumes appear in some of the earliest publications of the agricultural experiment stations. Indeed, some actual tests of the fixation of nitrogen by inoculated legumes had been made, notably those of Atwater, confirming Hellriegel and Wilfarth's work, but practically nothing else in the way of real scientific studies of soil microorganisms had been reported until just about the beginning of this century.

The work of Jacob G. Lipman, begun as a graduate student at Cornell University and continued at New Jersey, where he formed the first department of soil chemistry and bacteriology in the country, the investigations of Frederick D. Chester in Delaware, the studies on the legume bacteria and inoculation under George T. Moore at the Bureau of Plant Industry, and the work of

F. L. Stevens and W. A. Withers in North Carolina marked the actual beginning of soil microbiological research in this country. The publications of these investigators and of those of a few others which appeared in the very first years of the century stimulated and largely guided the extensive studies on soil microbiology which were conducted in the United States during the first two decades following 1900.

The problem of the nitrogen nutrition of plants had engaged the attention of the early agricultural chemists and was the subject of extended and often bitter controversy for many years. The mineral theory of plant feeding developed by Liebig in 1840 and the inescapable conclusion from the early experiments that plants could not use the nitrogen of the atmosphere but must have a supply of mineral nitrogen in the soil, led naturally to the development of the theory and practice of fertilization of the land with mineral fertilizers. In spite of the discovery of the ability of legumes, when well-inoculated, to draw upon the free nitrogen of the air, the problem of nitrogen fertilization was the subject of serious attention, and Liebig himself predicted that nothing would more certainly consummate the ruin of England than the scarcity of fertilizers, which would lead to a lack of food. It seemed evident to many that the exhaustion of the nitrate of soda deposits in Chile would mark the end of artificial nitrogen fertilizers and this would inevitably mean the end of the world. Indeed in 1898 Sir William Crookes in an address before the British Association for the Advancement of Science predicted that a scarcity of wheat would occur after 1931 and England, along with all other bread-eating nations, would be faced with famine unless the inexhaustible supply of nitrogen in the atmosphere could be transformed to nitrate fertilizer by electricity, to supplement the inadequate nitrate of soda deposits and maintain the nitrogen in the soil. He concluded that this was quite possible.

It was natural, in view of the general apprehension of a nitrogen shortage for food production, and also because of the interest in the problem of the nitrogen nutrition of plants, that the attention of the early soil bacteriologists should be more or less centered upon the relationship of microorganisms to nitrogen. Thus the great majority of the early studies involved the so-called "nitrogen" bacteria. The organisms that bring about the inoculation of legumes and enable them to utilize the free nitrogen of the atmosphere and the whole problem of legume growth and inoculation quite naturally were studied extensively both in the United States and abroad at the turn of the century, and the other nitrogen changes brought about by microorganisms, notably ammonification, nitrification, and nitrogen fixation, received almost as much attention, or perhaps even more, from the soil bacteriologists. The practical goal of much of the work was the solution of the problem of supplying nitrogen for future crops or the utilization of atmospheric nitrogen to build up and maintain the supply in the soil.

The work on the legume bacteria and on inoculation was concentrated mainly upon the development of pure cultures which would insure thorough

inoculation of legumes in the field and hence provide for a fixation of atmospheric nitrogen. Since the pure culture, Nitragin, put on the market in Germany by Nobbe had not given very satisfactory results, Moore and his associates attempted to develop new methods of culture that would give better inoculation, for it seemed obvious that inoculation with soil could hardly be depended upon and the various difficulties incident to its use overcome. The cotton culture method was devised and extensively tested around the country but unfortunately it was not so successful as had been hoped, and Chester showed that the difficulty with it was due to the inability of the organisms to withstand the drying on the cotton. Since reports from various stations bore out this conclusion, attempts were made to develop other types of cultures. It is undoubtedly true that much of the early pure culture inoculation failed because the cultures contained weak, inefficient bacteria or the wrong kind of organisms or perhaps only dead cells when the cultures were finally used. But in many cases the difficulties in the field tests by farmers were certainly attributable to the fact that other precautions in preparing the soil for the legume growth, such as liming, had not been observed. Even where everything possible was done, however, the cultures still, all too often, gave no benefits.

So the study of the legume bacteria has continued, and although the production of cultures has been developed on a commercial scale in recent years and successful inoculation generally follows their use, there are still some failures and difficulties in connection with inoculation. Some agricultural experiment stations still produce cultures which are distributed to farmers, apparently considering that they can produce better cultures than the commercial companies. But most of the investigators now are content to delegate culture production to commercial interests and devote their attention to the organisms themselves, realizing that further improvements in cultures must come from additional research on the bacteria and their characteristics.

The studies on *Rhizobium* in this country have been extensive, and much progress has been made in answering the questions of its morphology, its physiology, its cultural characters, its cross-inoculation relations, its inoculating power or efficiency, and its nitrogen-fixing power, and we are now approaching a solution of the problem of the mechanism of nitrogen fixation. At least six distinct species are now recognized, and characteristic physiological and cultural reactions are available for their differentiation. Certain definite cross-inoculation groups are distinguished, and the inoculating efficiency of various strains is recognized as important. The occurrence of a life cycle of the organisms has been demonstrated and a relationship to inoculation shown.

The actual amount of nitrogen fixed by well-inoculated legumes is still a matter of conjecture, however, in any individual case and probably varies widely depending upon all the conditions of the test. It is even believed that in certain cases inoculated legumes may fix no nitrogen at all. This, however, still remains to be proved. The fixation of nitrogen by the organisms when

grown alone, although studied in many experiments, is still an open question. The longevity of the various species in the soil has not yet been determined and probably never will be, for undoubtedly the conditions in the soil play a vital part in such a determination. Recent studies have indicated this fact. Sporadic attempts in the past to determine the occurrence of the organisms in the soil have been only partially successful, but recently a technique has appeared which merits further study and may serve as a means of determining the need for inoculation.

Further work on the physiology of the bacteria is necessary especially in connection with the differentiation of strains in order to provide a better knowledge of inoculation. Research to check on the life cycle of the organisms and on the relationship of the various stages of growth to inoculation is needed. Additional investigations are very desirable to determine the character and occurrence of fixation of nitrogen under known conditions. In short, although enormous progress has been made in the study of the symbiotic nitrogen fixation process since 1900, there is still much to be done and more complete and far-reaching investigations are sorely needed.

The non-symbiotic nitrogen fixation process was the subject of the early work of J. G. Lipman at New Jersey. Following the claims of Berthelot and the isolation of *Clostridium pasteurianum* by Winogradsky, Beijerinck in 1901 isolated and described two aerobic non-symbiotic nitrogen fixers and called them *Azotobacter chroococcum* and *Az. agile*. Lipman in 1903 isolated three additional species, *Az. vinelandii*, *Az. beijerinckii*, and *Az. woodstownii*. He also studied the conditions under which these organisms develop and pointed the way toward a more definite knowledge of their occurrence and action in the field. Much work has been done on this important group of organisms, a few additional species have been added and attempts have been made to inoculate soils in the field with pure cultures and thus bring about a fixation of nitrogen. These latter tests have all failed, and the commercial exploitation of cultures of supposed nitrogen fixers has involved some police work in certain states to protect farmers from unscrupulous salesmen of these spurious products. It is certain that some day there will be a method developed for inoculating soils with *Azotobacter*, but much work is necessary before this can be done. Much progress is being made in the study of the physiology and cultural characteristics of the organisms and the determination of their nitrogen-fixing power or efficiency. The results of these investigations will aid in the solution of the problem of utilizing these organisms practically. Extensive work on the conditions in the soil under which the organisms make their best growth, has paved the way for a more detailed study of the organisms and their activities and for a solution of the problem of adding to the nitrogen of the soil by encouraging their growth or adding them to soils not containing them. There has been a vast amount of worthwhile work on this group of organisms following Lipman's lead in this country, and the future holds promise of further and still more important results from such work.

The studies of Lipman, Chester and Stevens, and Withers initiated the extensive experiments in this country on the determinations of numbers of organisms in soils and the activities of various groups of nitrogen-transforming organisms known as the ammonifiers, nitrifiers, and denitrifiers. Chester studied the numbers of organisms in various soils under different conditions; in spite of the inadequacy of the medium employed and the limitations of the tests, his conclusions regarding the occurrence of bacteria in soils and the effects of various factors upon them are still largely supported by later, more extensive studies with presumably better techniques.

Chester made the first so-called bacteriological analysis of soils and in addition to numbers he determined their so-called "zymotic" efficiency or ability to bring about the formation of certain specific products of decomposition. He emphasized the fact that a knowledge of the numbers of organisms in soils is not sufficient but it is also necessary to have information regarding the activities of the organisms to learn anything of their relation to fertility or crop production.

Lipman at New Jersey developed the study of the activities of various physiological groups of organisms in soils, devoting some attention to numbers, however, and developing the synthetic medium for counting bacteria, modifications of which have been used in all the later studies of numbers by plate counts. Lipman early emphasized the fact that the importance of microorganisms in the soil was due to their action and not necessarily to their numbers. His work and that of Stevens and Withers began with the use of the Remy method which had just appeared, and with this method and some modifications of it, extensive studies on ammonification, nitrification, denitrification, and nitrogen fixation were carried out and some interesting and suggestive conclusions were drawn. But difficulties with the method were soon encountered, the chief of which was that it did not permit of a fine enough bacteriological differentiation between soils. About 1909-1910 Lipman suggested the soil or tumbler method at almost the exact time that Stevens and Withers reached the conclusion, from their nitrification studies, that soils must be employed in tests of that process to give an accurate picture of what was occurring in the field. It is interesting to note that tests in soils were first suggested abroad at almost the identical time by Lemmerman, Fischer, Kappen and Blanck, Koch and Petit, and Vogel but work with the method developed more rapidly in this country than in Europe.

Lipman, and Stevens and Withers emphasized the importance of the chemical as well as the bacteriological factors in controlling such processes as nitrification in the soil. Stevens and Withers suggested the terms "N.C." and "N.I.P." for nitrifying capacity and nitrifying inoculating power, representing the same thing as Lipman's chemical and bacteriological factors. The sum of N.C. and N.I.P., Stevens and Withers called "N.E." or nitrifying efficiency. Lipman merely called this the "nitrifying power" of the soil. Similar terms were suggested for ammonification. But although Stevens and Withers'



terms never came into use, in all later work the importance of using soil for testing the activities of microorganisms was clearly recognized.

Lipman's studies embraced ammonification and nitrification, and, in addition to the further development of techniques, considerable information was obtained regarding the occurrence of these processes in field soils and their relation to fertility. He and his coworkers studied the conditions affecting the processes and gathered many facts of technical and practical significance. Lipman also studied denitrification and some of the organisms responsible for the process, following up the studies of Voorhees along this line, which had indicated that the occurrence of the process under field conditions was highly improbable.

As a result of these early studies, bacteriological investigations of the activities of microorganisms in the soil in transforming nitrogen compounds began in various sections of the country, and much valuable information was accumulated. Emphasis has been placed upon the relation between these significant bacteriological processes and the fertility of soils, and it has been found that the character or vigor of these processes in soils may indicate fertility or producing power. In fact, this is usually true, particularly in the case of nitrification. But these investigations, if they did nothing else, very soon led to a general recognition of the dynamic character of soils, a thing which had not been appreciated before and which is most significant in connection with soil management practices and permanent fertility methods.

Lipman in his earlier work also demonstrated the importance of the associative growth of inoculated legumes with non-legumes and found, as did others, that nitrogen may be supplied to non-legumes when they are seeded with inoculated legumes. This work has, of course, a direct bearing on the whole problem of nitrogen fixation by legumes, the methods of fixation, and the form in which the element is fixed.

Mention should be made also of the review of soil bacteriological investigations by Voorhees and Lipman published in 1906 by the Office of Experiment Stations. This summarization and analysis of all the work along soil bacteriological lines did much to stimulate the work in this country.

The pioneer studies of Lipman, Chester, Moore, and Stevens and Withers in the United States certainly have led directly to all the important investigations of symbiotic and non-symbiotic fixation of nitrogen, ammonification, nitrification, and denitrification and of the numbers and kinds of microorganisms in the soil. They have also led to the recognition of the relationship between bacteria and soil fertility or crop production and a permanent agriculture. But this is only a small part of the story. Other developments of the science, almost too numerous to mention, and many of them of almost as great significance have come about indirectly as a result of the inspiration or suggestion derived from these early studies.

The extensive work in this country on cellulose decomposition and more recently on the breakdown of various non-nitrogenous compounds and even

lignins, by microorganisms, may be mentioned. It is very significant. The development of the study of molds, actinomyces, algae, and protozoa has been remarkable, the first two groups of organisms receiving most attention in this country while the algae and protozoa have been studied mainly in England and to a lesser extent over here. Carbon dioxide production in soils has received considerable attention both here and abroad, and its importance as a measure of decomposition processes in the soil and as an indicator of soil fertility has been definitely proved. Methods of studying the carbon dioxide produced under varying conditions have been developed, and the effects of different factors on the process have been determined.

The study of sulfur bacteria and their activities in soils has been carried on to some extent. It has been shown that soils have a sulfur-oxidizing power which is dependent upon various factors peculiar to them. The question of sulfur fertilization of the land is involved here, and the process of sulfonation may become more important in the future, if or when sulfur fertilization becomes a common farm practice. The studies of Lipman and his colleagues on sulfur-rock phosphate composts, besides indicating a method of making a soluble phosphate, suggest much regarding reactions in the soil following the use of sulfur as a fertilizer. Data regarding the sulfur oxidizing bacteria were also obtained in connection with this work.

The importance of microbial actions in making phosphorus available in soils has been investigated. It appears that there is a definite relationship between certain microbiological activities and the production of the element in an available form, from different phosphorus compounds in the soil and from various fertilizer carriers of the element. The phosphorus requirements of microorganisms have been studied, and certain methods for determining the need of soils for phosphates have been based upon the sensitiveness of such organisms as the *Azotobacter* and *Aspergillus niger* to a deficiency in available phosphorus. The effects of applications of phosphorus carriers upon microorganisms have been shown, indicating that such fertilizers have indirect as well as direct effects upon the fertility of the soil. Other fertilizers have also been studied to determine their relationship to microorganisms. Potash fertilizers, various nitrogen carriers, and certain complete commercial fertilizers have all received attention, and important microbiological changes have been found to occur in soils following their application.

Methods of study have received much attention, and many advances along this line have been made. The development of the microscopic method for determining numbers and kinds of organisms in soils is one of the most significant. Although there is still a definite recognition of the limitations of studies of numbers, many interesting data have been obtained by this method, and further work along this line may lead to many more discoveries of the kinds of organisms in the soil. Mention should also be made of the study of anaerobes which has been under way in recent years. The possibilities of these organisms' functioning in important processes in soils are indicated.

No attempt has been made to indicate all the soil microbiological investigations that have been conducted in the United States during the past 35 years but merely to list the more important phases of the science which have received more or less attention and on which considerable significant data have been obtained. Certainly sufficient results have been mentioned to indicate the great development of the subject of soil microbiology since its beginnings about 1900 in the work of Lipman, Chester, Moore, and others.

It is true that the science attracted most attention both in the United States and abroad early in this century and it may have seemed to many in recent years that there has been less attention to the subject than it deserved. Indeed Waksman in 1925 reported considerable pessimism both in this country and in Germany regarding the development and possibilities of the science. It was pointed out that by 1903-1904 the most significant microbiological processes had been discovered and the causative organisms had been isolated and described and since then no new processes have been found. This is true in the main, but the chief reason for the falling off of interest in the science was the fact that the important results of the studies in medical bacteriology had led many to expect similar radical and far-reaching effects of soil bacteriological research upon practical agriculture. When these expected results of the early studies did not appear and when, outside of legume inoculation, few practical results were suggested, many scientists and practical agriculturists were vastly disappointed and lost interest in the subject. Just why a science should be required to revolutionize existing practices to be considered of significance is difficult to say. And yet that seems to be the attitude of many investigators, some of whom should certainly have a better conception of the real measure of the value of scientific studies and a sound basis for evaluation of such studies.

Furthermore, a lack of appreciation by the workers in the field or by outsiders of the practical application of research results certainly does not mean that the data do not, or may not in the future, have some extremely significant effects upon practice. It merely means that these people cannot yet see the application. Some of the most significant scientific discoveries have remained hidden for years before their practical importance has been recognized.

And then there are those who still claim that nothing new has been added to the science, no new methods have been developed, no new processes discovered since the early days of 1900. Again these are people who are not fully acquainted with the science or who are looking for something new and startling and fail to recognize the potentialities of the results which are being obtained. They seem to expect the startling discoveries of the early studies of a new science to be continued indefinitely. In other words, they expect the impossible.

A careful study of all the work that has been done since soil microbiological investigations began in this country will certainly convince any who are willing and able to analyze the situation that really amazing progress has been made

and that soil microbiology has been put upon a sound basis as a science. The work in this country and abroad has developed in a sound and conservative way, and the brilliant beginnings of the science have been followed by the careful accumulation of facts, the confirmation of the early suggestions, and the broad interpretation of the results. The usual scientific method has been followed, and the results have been gratifying to those who because of thorough interest in the subject and appreciation of the complexity of the science and its ramifications are really soil microbiologists.

All honor to those pioneer students of the science of soil microbiology in this country! They initiated work of great interest and practical value. They provided the foundation for a real science. And the end is not yet. The recognition of the soil as a place of life, as a dynamic thing, is general now as a result of the work of the soil microbiologist. This would be sufficient to justify all the work on the science, if nothing else had resulted. At the present time when national attention is directed to soil conservation and the establishing of a plan for the agriculture of the future it is particularly important that the true character of the soil and the occurrence and activities of microorganisms in it should be recognized and appreciated. And who can predict the results of the future and their value or the practical applications of the work of the past, which may come at any moment?

Soil microbiology is a science of great significance at present and it will continue to be just as important in the future and will, perhaps, become more important. But there is need for more and more study of this fascinating and important science. Much remains to be learned of the processes in the soil, of the relationships between various microorganisms, of the dependence of the organisms upon soil conditions, and of the relations of the different processes to crop growth, to soil conservation, and to permanent agriculture. It is certainly to be hoped that administrators will be sufficiently far-sighted and alert to the true situation, to see to it that investigations along this line are continued and developed and that teachers and research workers in the field will be enthusiastic and inspiring enough to induce some promising young investigators to enter the intriguing field of soil microbiology.

# THE METHOD IN SOIL MICROBIOLOGY AS ILLUSTRATED BY STUDIES ON AZOTOBACTER AND THE NITRIFYING ORGANISMS

S. WINOGRADSKY

*Pasteur Institut, France*

Received for publication December 10, 1934

Nearly ten years have passed since the writer first tried to draw attention to the conventionality of the methods applied in soil microbiology. He pointed out that the evidence required in soil microbiology cannot be founded on the classical pure culture method as trustfully as in the case of chemical, industrial, or medical microbiology. Pure cultures of organisms, isolated years ago from the soil, grown on artificial media for an unlimited time on nutrients essentially different from those the original wild species might find at their disposal in the soil, severed for countless generations from the biological conditions of the soil—these cultures cannot tell us much about microbial activity in nature. The utmost the classical method can give us is a few conventional notions only vaguely outlining what really happens.

To improve the method in soil microbiology, the author made the following suggestions:

- (a) Avoid, on principle, working with stock cultures.
- (b) Use for experiments strains freshly isolated from the soil by a method as short and direct as possible.
- (c) Supply them with nutrients that can be supposed to be utilized by them in the soil.
- (d) Make a special point of studying the reactions of the soil population as a whole, since the competition between its components is the principal determinant of their individual functions.

For these experiments a solid mineral medium was recommended, chemically inactive and perfectly suitable as a vehicle of nutrients for soil organisms: silica jelly.

The writer is ready to admit that considerable progress has been made in leading laboratories since these suggestions were first put forward. Nevertheless, he believes that much remains to be done in this direction, that is, in working out a method more closely adapted to the aims and problems of soil microbiology which center round microbial activity in its natural environment.

To illustrate his point of view, the writer proposes to review critically the methods and results of recent researches on *Azotobacter* and the nitrifying organisms.

## THE SUGAR AZOTOBACTER AND THE SOIL AZOTOBACTER

For the past thirty years, ever since Beijerinck discovered *Azotobacter*, it has been grown on sugars, because these substances give the richest cultures. The strains fed on sugar for an unlimited number of years are used for physiological experiments, which always, or almost always, are carried out on sugars, in spite of the fact that since Beijerinck's time *Azotobacter* has been shown perfectly capable of living on substances of inferior nutritive value. Apparently, microbiologists did not trouble to replace a standard medium by others and thereby risk obtaining poorer cultures. Indeed, from a technical point of view heavy growth seems an achievement, but the agrobiologist has a right to doubt whether in nature the original strain ever has the opportunity to be overfed in a similar way, and whether this overfeeding might not in the long run modify the characteristics of the cultivated strain, particularly its metabolism.

Let us say at once, that the use of glucides as nutrients was not a happy idea from an agrobiological point of view. It has led to a complete misunderstanding of the conjuncture of the activity of *Azotobacter* in the soil. As Waksman rightly remarks:

Nevertheless, there is one point not yet settled, namely, whether these organisms (*Azotobacter*) really fix nitrogen in the soil under field conditions. This has been emphasized by the fact that available energy is not supplied in the soil in the form of mannitol or dextrose universally used in the study of pure cultures . . . but rather as cellulose and other complex carbohydrates, which these organisms are quite unable to use as a source of energy.<sup>1</sup>

For there is no doubt that in their natural environment these organisms never find the opportunity to feed on sugar or mannitol, and that most certainly they derive their energy from very different sources. If such is the case, one is led to suppose that laboratory strains cultivated for innumerable generations on sugars may well have acquired functional characteristics different from those of the corresponding wild strains.

The divergence in the aims and ideas in general microbiology and agricultural microbiology is again made evident by the question of nitrogenous nutrition of *Azotobacter*. Ever since the beginning of researches on this organism it has been shown that growth occurred more easily on a medium containing combined nitrogen than on a medium lacking it. This became a second way

<sup>1</sup> Translation from the German text: "Jedoch eines ist bis jetzt noch nicht festgestellt worden und zwar das, ob diese Organismen (die *Azotobacter*) unter Feldbedingungen wirklich Stickstoff im Boden binden. Das ist ferner durch die Tatsache betont worden, dass die dem Boden zugeführte Energie nicht in Form von Mannit und Dextrose, die beim Studium der Reinkulturen allgemein gebraucht werden . . . zugeführt wird, sondern als Cellulose und andere zusammengesetzte Kohlenhydrate, die von diesen Organismen ganz und garnicht als Energiequelle gebraucht werden können. . . ." *Methoden der mikrobiol. Bodenforschung*.—*Abderhalden Handbuch der biologischen Arbeitsmethoden*, p. 718. See also: *Der gegenwärtige Stand der Bodenmikrobiologie etc.* Abderhalden: *Fortschritte der naturwissenschaftlichen Forschung* 10 (1930): 72.

to stimulate its vegetation. The question of how *Azotobacter* utilizes the different forms of combined nitrogen has been extensively studied. Undoubtedly, it deserved the attention paid to it, but the conclusions that certain authors (Bonazzi, Dean Burk) have drawn from their observations are contrary to reality. They hold, namely, that *Azotobacter* is an organism which *normally* feeds on combined nitrogen and that it takes to fixation of molecular nitrogen only when artificially forced to it by nitrogen starvation, whereas it has been experimentally proved that in a soil containing combined nitrogen *Azotobacter* is repressed by rival organisms until it is crowded out and finally smothered altogether (6).

This question will be resumed later in this discussion.

To recapitulate, one is inclined to agree with Waksman in that all research work from Beijerinck's time to 1930 has failed to make the rôle of *Azotobacter* in the soil any better understood.

#### THE MANOMETRIC MICRO-METHOD

In the course of recent years considerable attention has been attracted by the new manometric method, initially worked out by O. Warburg for the study of cellular metabolism. It was Dean Burk who applied the technique to a nitrogen fixing organism for the first time. In his papers he repeatedly points out the advantages of this physicochemical quantitative micro-method over the older chemical methods, which involved nitrogen and sugar analysis: since the experiments with them usually required several days or weeks, it was impossible to maintain constant reproducible conditions. "The ambiguous effects occurring in the case of old and heavy growths, such as . . . relative lack of nutrients, or complicated mixtures of various stages of life cycles, are avoided." Whereas, with the new technique, "the manometers can be read very frequently . . . growth and respiration can be determined over very short periods of time (minutes and hours . . . with an accuracy considerably greater. . . . In view of the young and highly diluted culture used, one is concerned chiefly with constant, reproducible and, one might say, ideal conditions. . . . One is concerned with the differentials and not only with the integrals of cell metabolism . . ." (1, p. 1177).

The writer has quoted from Dean Burk's papers, in order to use his arguments in favor of the new method (1), which are convincing as far as they concern cell respiration and cell metabolism. Expertly handled by Dean Burk and others, the new method has led to some remarkable contributions, such as the importance of calcium for the fixation process, the rôle of humic acid in making iron available, and the relation between respiration, growth, and nitrogen fixation.

Fully aware of the advantages of the new method where problems of physiological chemistry are involved, the agrobiologist, nevertheless, ventures to inquire whether the new method will bring us any nearer to solving the problem of the activity of *Azotobacter* in its natural environment than did the old one, which has left it at a dead point.

The writer thinks the answer is in the negative. If anything, there is even less chance of coming nearer the required solutions by the new method than by the old one. The reason for this is of itself obvious. In the new method stock cultures are used for the experiments, which are performed with sugar as nutrient and with pure cultures exclusively, eliminating thereby biological conditions just as in the old method, with the difference that here only young cells are dealt with, and, furthermore, these are shaken up continuously during the short time the experiment lasts. The conditions, perfectly uniform as they are, appear too narrowly limited and artificial to allow for investigating the functions of the organism more or less completely. Even taking for granted that an *Azotobacter* cell possesses reactions peculiar and inherent to its protoplasm, still one cannot go so far as to admit that they are absolutely independent of external conditions; otherwise, this would mean a negation of the long established fact of morphological and physiological variation under the influence of these conditions.

With these considerations in mind, the writer would prefer to keep to the general lines of the old bacteriological method, the real object of which is the integral function, rather than the differential, and this by using a method based on the principles indicated in the foregoing.

Finally the writer would like to lay stress on the fact that the true character of the activity of *Azotobacter* will never be revealed by chemical and physico-chemical means alone, without taking the biological factor into consideration; that is to say, without studying the behavior of this microorganism in its natural environment as part of the microflora of the soil as a whole. This side of the question has not had the good fortune to attract much attention. We will begin with it.

#### CONDITIONS AFFECTING THE ACTIVITY OF AZOTOBACTER IN THE SOIL

The first observations on the subject date from 1926, (6) and were carried out by the following simple method:

To 50 gm. of sifted soil from a freshly taken sample 0.5 gm. of mannitol is added and the whole well mixed, moistened as required, and spread in a Petri dish so that the layer is about 1 cm. thick. The sample having been previously studied microscopically, the appearance presented by its bacterial population is known, which makes it easy to detect the new growth as soon as it appears after the addition of mannitol. The density of the microorganisms can also be roughly estimated by the writer's microscopic quantitative method described elsewhere (5). It will be observed that the biological reaction in this case nearly always starts by a growth of bacilli attaining a density in the medium of several tens of millions in the first 24 hours at 30°C. This first growth is markedly more abundant in the case of a fertile soil than in that of an unfertile one. After 48 hours, however, the appearance of the culture will be found to have changed considerably: the bacilli will now be difficult to find, as they are crowded out by *Azotobacter*, of which the density can roughly be estimated at several hundreds of millions per gram of soil. During the third and fourth day the *Azotobacter* growth reaches two to three billions per gram. The soil and soil solution are filled by the organism, and the earth particles are coated with its mucilage.



These and similar observations lead to the conclusion that if energetic material containing no available nitrogen is added to a well-aerated soil, it has the effect of stimulating *Azotobacter* growth only, almost all the other parts of the bacterial population remaining at rest. A bacillary form seems to make an exception to this rule, but its scanty and short-lived growth has the evident effect of using up any trace of combined nitrogen the soil might have contained. These are precisely the conditions most favorable to *Azotobacter* growth. All other species being now eliminated from competition because of the lack of available nitrogen, the organism can avail itself of all the nutrient and multiply freely.

The correctness of this interpretation is further proved by a similar experiment, where small quantities of nitric nitrogen were added to five 50-gm. portions of soil in five dishes, in the following percentages of nitric nitrogen to glucose (5):

(a) 0, (b) 0.5, (c) 1.0, (d) 1.5, (e) 2.0.

The results were as follows:

- (a) Density of *Azotobacter* growth after 72 hours, 2 billion per gram of soil.
- (b) Abundant growth of bacilli. After 48 hours *Azotobacter* appears, starting with a few individuals, attaining a density of 75 million per gram of soil after 72 hours.
- (c, d, e) All three portions crowded with bacilli only. *Azotobacter* does not appear at all.

The foregoing experiment shows decisively that the presence of very small quantities of combined nitrogen has the immediate effect of altering the whole nature of the bacterial population of the soil: the smallest dose of nitrogen added—5 per 100,000 the weight of the soil—was sufficient to retard the growth of *Azotobacter* and reduce its density to  $\frac{1}{25}$  of what it would be without the addition of nitrogen; whereas larger quantities suppressed all development of this fixation agent (6).

In 1932, the author resumed the question while working out a general method for studying the biochemical activity of individual organisms or groups of organisms belonging to the soil population without dissociating or isolating any of them (9). Silica-jelly plates impregnated with different nutrients were simply sprinkled with soil particles. One part of them received fixed nitrogen, the other did not. *Azotobacter* colonies appeared only on the second lot, the first showing diverse vegetation but never any *Azotobacter* growth. This happened unfailingly with every kind of energy-supplying material used.

If, as it follows from these two sets of experiments made by means of two different methods, *Azotobacter* can hold its own only in soils where available nitrogen is scarce or lacking, then nitrogenous fertilizers of any kind would be inimical to its growth in the field. Regular and abundant dressings would tend to reduce its density or even make the species disappear altogether.

The writer knows of only two attempts to investigate the foregoing question. One was made by himself with Madame Ziemięka (7); the other, by Madame Ziemięka independently, using the same method (12).

Ten samples from the Experimental Vine-Growing Station at Grammont near Montpellier were sent to the laboratory under their plot numbers, but with no indication as to treatment received by them. The question on hand was to determine the density of *Azotobacter* in these samples (known to harbor this organism) in relation to the treatment received by the plots. The following counts were obtained on large silica-jelly-mannitol plates (20 cm. diameter):

<i>Number of plot</i>	<i>Count per gram of soil</i>
3	12,000
4	2,000
21	600
6	500
9	420
8	400
2	360
12	170
16	60
18	0

The treatments to which the plots had been subjected for 6 years follow: Number 3 was dressed with mineral fertilizers only, none of which contained nitrogen. Number 4 is a control plot, and had had no dressing at all. The rest of the ten plots received yearly 80 kgm. of nitrogen per hectare—40 as dried blood, 20 as powdered horn, and 20 as potassium nitrate.

The counts show the harmful effect of nitrogenous fertilizers.

In the three last plots ammonium sulfate was used instead of the nitrate, causing a degree of acidity sufficient in this poorly buffered soil to strike the last blow to the *Azotobacter* population, which in Number 18 falls to zero.

More extensive tests were carried out by Madame Ziemięka (12) on the classical fields at Rothamsted, which afford, as the author acknowledges, "a unique opportunity for testing methods of microbiological soil analysis, since on them results can be correlated with manurial treatment and with yield data extending over a longer period than is obtainable elsewhere." In all, 79 samples were tested, all taken from the Rothamsted plots. The samples from Broadbalk, especially, were examined three times in the most thorough manner possible. "The best conditions for *Azotobacter* growth on all three occasions were found in plot 5," says the author, "which received complete minerals but no nitrogen. . . . The most striking feature of Broadbalk samples was the repression of *Azotobacter* in plots receiving mineral nitrogen. . . . The counts made on silica-jelly show an inverse relation between the *Azotobacter* numbers and the nitrogen dressing. Even on the dunged plot the number of *Azotobacter* colonies was much reduced and was lower than the control plot when the latter's phosphate deficiency was made up."

Since tests of samples from other fields at Rothamsted gave similar results,

the writer is led to make the general conclusion that in soils treated with 86 pounds or more of mineral nitrogen, the test usually showed little or no Azotobacter growth, even in the presence of phosphate and calcium carbonate; this failure was probably due to the paucity of Azotobacter cells, originally present in such samples.

Here, then, is an instructive example of an error which disregard of biological conditions may lead one into making. Molecular nitrogen, the observer thinks, is not essential to Azotobacter, since this organism grows much better on fixed nitrogen. This might come to be considered as the *normal* condition for its growth. Conversely, growth is slower when the organism is obliged to assimilate nitrogen gas, this latter case might then be considered as *abnormal*. In nature, Azotobacter is forced by bacterial competition into leading this hampered existence almost constantly, for only in this way can it appropriate its part of the energy-supplying material. The reason for this easily verified fact is to be sought in its rate of multiplication, which is much slower than that of the bacilli. Consequently, Azotobacter can avail itself of the nutrient only when multiplication of its antagonists is paralyzed by the lack of nitrogenous compounds. In other words, the biochemical forces of the soil come into play, starting to fix nitrogen only when the soil becomes poor or deprived of nitrogen compounds, but the process is arrested as soon as the rate of the nitrogen fixation reaches a certain level, always relatively low.

This law, when confirmed as such, will perhaps one day make the farmer think over the fact that in paying for the nitrogen in fertilizers he deprives his land of nitrogen which nature gives him for nothing.

This lagging behind in the competition with other organisms must be considered a marked negative characteristic, because of which the organism has to feed on nutrients of inferior quality. As can be seen from the evidence on the decomposition of vegetable matter in the soil, brought out by Waksman, soluble carbohydrates accompanied by proteins, amino acids, or even ammonia and nitrates are very rapidly decomposed in the soil, and it appears certain that the bacilli alone bring about the process as long as the supply of complete nutrients, i.e., available carbon with a suitable proportion of available nitrogen, is not exhausted. The process slows down when the turn of the vegetable skeleton comes—cellulose, hemicellulose, lignin—and it is at this moment that available nitrogen becomes scarce. Vegetable matter is poor in nitrogen, which is then drawn from the soil, thereby creating areas very poor in, or entirely deprived of, available nitrogen but rich in the usual waste products of fermentation—fatty acids and alcohols—, of which Azotobacter is left in sole possession. Because the medium lacks available nitrogen, no other organism can dispute them. Hence the conclusion appears inevitable that these waste products are the usual nutrients used by Azotobacter in the soil. Indeed, the organism is known to grow on them readily—though less abundantly than on sugar—, and to fix nitrogen.

The chemical energy of the organism seems extraordinary, when one con-

siders that it thrives on benzoic salts—a fact established by the writer—, showing abundant, typical, and pure growth. Whether benzoic acid occurs in the soil, as a waste product of lignin decomposition, for instance, is not known, but it is not improbable. This may or may not be, but the writer by the use of benzoic acid has devised one of the most efficient and direct methods for isolating *Azotobacter* from the soil, which will now be described.

#### THE BENZOATE METHOD

If the question does not go beyond making *Azotobacter* counts in the soil or controlling its capacity for nitrogen fixation, mannitol and sugar are almost as good as, or sometimes better than, any other energy material. But they are not suitable where direct and rapid isolation of the organism in a state of purity is required for use in experiments on biochemical questions of the kind about to be discussed. As is known, *Azotobacter* growth on sugar and mannitol is never pure, and, consequently, repeated replating and reinoculation are indispensable. The use of a micro-manipulator on mixed material does not help much to get rid of impurities. Therefore, if stock cultures are to be avoided, direct isolation from the soil can be successful only with the most selective medium. The author thinks benzoic salts are best suited for the purpose.

Pure commercial sodium benzoate and calcium benzoate, free from salicylate, recrystallized once or twice may be used. The doses of the salts are as follows: sodium benzoate, 0.1 gm. to 30 cc. of silica-jelly in a 10 cm. diameter Petri dish; 0.5 gm. of the salt to 150–200 cc. silica-jelly in a 20 cm. diameter Petri dish. For calcium benzoate the doses are smaller: 0.05 gm. and 0.3 gm. respectively.

It is not advisable to raise the dose beyond the figure indicated. To keep solutions of these salts ready for use will be found convenient, the concentration being: 0.1 gm. sodium benzoate or 0.03 gm. of calcium benzoate to 1 cc. of solution.

Further details about the preparation of the plates are given elsewhere (1, 9).

They are inoculated with a very small quantity of soil from a sample known to harbor *Azotobacter*, by sprinkling the soil particles over the whole surface through a Gooch crucible. The crucible can be weighed before and after the operation to ascertain the exact weight of the soil used, should this information be needed. This weight ought not to exceed one to a few centigrams.

Conspicuous colonies of *Azotobacter* appear during the second day of incubation at 30°. Examined under the microscope without delay, they will be found to consist of both the larger and the smaller forms of *Azotobacter*, the majority quite pure, others containing a few isolated rods. When the best colonies are picked out, they must be reinoculated at once in order to get rid of amoebae, which would otherwise multiply and ravage the cultures.

Sometimes, in order to have inoculation material ready to hand, and also with a view to economizing plates, it will be found convenient to inoculate

some liquid cultures. The composition of the solution is similar to that of the plates: namely,

Calcium benzoate.....	10 cc. = 0.3 gm. of
Nutrient salts solution.....	10 cc.        the salt
Solution of humates.....	10 cc.
Tap water.....	170 cc.

Fifteen cubic centimeters of this solution to a 125-cc. Erlenmeyer flask will form a layer a few millimeters deep.

For nitrogen fixation and other experiments, pure colonies sprung up round the earth particles are used. A suspension of them is made in sterilized tap water, and enough of this is poured over the plate to moisten the whole surface. When control plates are necessary, they are given the same quantity of suspension and immediately treated with chloroform vapor in a closed receptacle. This way of inoculating over the whole surface has the advantage of shortening the time the plates need be kept, which must not exceed 96 hours. Mannitol or calcium lactate silica-jelly plates can be inoculated in an exactly similar way in cases where particularly heavy growth is required for subsequent analyses.

The development of the organism on benzoate plates is quite regular and highly characteristic. Slightly milky at first, the colonies grow opaque with age and take on a chocolate-brown color after 3 or 4 days, the whole of the jelly turning a smoky black.

These features are particularly pronounced when the plate carries only a few colonies, for when a sodium benzoate plate is entirely covered with *Azotobacter mucilage* the jelly becomes slightly liquefied because of the alkalinity of the medium.

Under the microscope during the first and second day the growth is seen to be composed of elongated cells in pairs or short chains; by the third day, rounded individuals are decidedly predominant; on the fourth, only rounded, blackened, and encapsuled forms are seen, which represent the resting stage of the organism. The general impression is of regular and normal development. Involution forms, frequent in cultures on glucides, are never found.

For analysis, the plates are put to dry, after the jelly has been flooded with 2 cc. 0.1 *N* HCl to avoid loss of ammonia. If they are to be Kjeldahlized, the scales of dry silica are transferred to a Kjeldahl flask and the dishes washed out with a minimum of water using a glass rod tipped with a policeman.

The nitrogen fixation on this medium was proved by the macro-Kjeldahl as well as by the micro-Kjeldahl method. The latter is certainly preferable; especially with the use of a Parnas and Wagner distillation apparatus, as recommended by Pregl. Difficulty is sometimes experienced when the dry silica to be burned exceeds the convenient volume for the capacity of a micro-Kjeldahl flask. In that case a macro-Kjeldahl is used, the product of combustion is made up to 100 cc. with distilled water, and 20-cc. portions of this are distilled.

The average figure for all determinations made is 11 mgm. of fixed nitrogen per gram of benzoic ions, i.e., a little more than in the case of mannitol and glucose cultures, where it is generally less than 10 mgm. under identical conditions.

To recapitulate, the writer believes that the benzoate method provides the means for operating with *Azotobacter* taken directly from the soil, and that with a better chance of its being pure and authentic than when taken from stock cultures.

Certainly, in the material thus isolated several strains may be mixed, and, consequently, further manipulations are needed if a particular strain is wanted. In the latter event it is best to have recourse to a micro-manipulator. If it be objected that it is less trouble to take ready stock cultures labelled *chroococcum*, *agilis*, *vinelandii*, etc. than to make a fresh isolation, the writer believes that the labels do not, by far, always correspond to the characteristics of the original species and that a thorough control of the apposed diagnosis is not often an easy task.

#### AMMONIA SYNTHESIS

The writer does not think it necessary here to review once more the history of ideas prevalent on the chemical mechanism of fixation. Suffice it to say that the synthesis of ammonia by direct combination of hydrogen and nitrogen—a hypothesis nearly a century old, for it was first advanced by de Saussure—, was considered by the majority of students most probable from a theoretical point of view. Does not the *model* of chemical industrial synthesis of ammonia based on catalytic action suggest an analogous process in the case of biological synthesis?

It must be admitted that the experiments performed during the last quarter of a century failed, in spite of their very great number, to find conclusive evidence to support this hypothesis until 1930. Traces of ammonia have been occasionally observed by some authors, but then they give no precise data as to the nature of this ammonia liberation or the conditions on which it depends.

Ammonia being one of the commonest products of decomposition, a different origin, even if probable, is not easy to trace. Without a very close microscopic examination of the culture it is not possible to decide whether ammonia liberation is the result of some degradation process, caused by attacks of foreign organisms or by cell autolysis. Then again, should any ammonia appear, to start determining it after the culture has been incubated for an arbitrarily fixed number of days will not help to decide whether it is produced by young, adult, or old, and perhaps degenerate cells. In papers published before 1930 these very data are missing. As to the origin and characteristics of the cultures used, only mention is made that they were stock cultures labelled *A. chroococcum*, *A. agilis*, *A. vinelandii*.

On this subject a paper by Kostytchew, Ryskaltchouk, and Schwezowa attracted most attention (3). The authors had found considerable quantities of ammonia and amino nitrogen in their cultures of *A. agilis* and did not hesitate to consider it as the first tangible product in the process of synthesis.

Do their experiments support this conclusion? The writer thinks not. It is enough to say that the fact that analyses of their liquid cultures were made after 10–15 days and even after 20–25 days makes the origin of the ammonia found quite uncertain. Nothing is said about the microscopic characteristics of the growth in their cultures. Did they find it pure after such a long period of incubation? Was it free from autolyzed cells? There is only mention that the stock culture used was labelled *A. agilis* and was obtained through the courtesy of a colleague. The quantities of nitrogen found in the solution were considerable, for example: one culture contained 13.4 mgm. total nitrogen, of which 12.4 mgm. was ammonia nitrogen; another culture contained 10.7 mgm. total nitrogen, of which 4.9 mgm. was ammonia nitrogen and 6.5 mgm. amino nitrogen. The presence of the latter was proved in all the cultures, and it is hard to admit that it is due to anything but the degradation of cell proteins. True, the authors insist on the analogy between reduction processes brought about by *Azotobacter* and the reduction of nitrates by molds, the products of which, ammonia and amino nitrogen, accumulate outside the cells only in the surrounding culture solution; this, they suppose, would be the case with the products of nitrogen fixation by *Azotobacter*.

If this were true, bacillary growth would easily crowd out *Azotobacter* growth under natural conditions, as has already been described. Now, nothing of the kind is observed on plates inoculated with soil. Similarly, according to Dean Burk's findings, *Aspergillus niger* does not grow in nutritive solutions after *Azotobacter* has been grown in them, unless traces of available nitrogen have been added to them.

Lastly, if the production of such noticeable quantities of ammonia is a regular phenomenon, an explanation must be found of the contradictory results obtained by the very great majority of investigators who have not detected any ammonia whatever. The contradiction would be easier to understand if a new culture method were applied more sensitive for the detection of ammonia production, but this was not the case, for the authors kept to the old standard method for growing *Azotobacter* in solution.

These criticisms have already been formulated in a communication made by the writer to the Académie des Sciences on March 17, 1930 (8). He insists that he has not observed ammonia production in his very numerous cultures on mannitol media, but he goes on to say:<sup>2</sup>

This negative result cannot be considered as a proof against the hypothesis of hydrogenation of molecular nitrogen, for it is enough to imagine a state of perfect equilibrium between the processes of ammonia synthesis and ammonia assimilation, to understand why it is not

---

<sup>2</sup> Author's translation from the French (8, p. 662–663).

detected in a free state. It is a question, then, in the present problem, as in others dealing with analyses of microbial processes of discovering the particular conditions which would throw the phenomenon out of equilibrium in order that we may intercept its primary products. This could be attempted in two ways; namely, by applying means to prevent the ammonia from entering into combination, or in repressing the plastic or assimilatory process in the cells. If the hypothesis of the hydrogenation of nitrogen through microbial activity is well founded, an accumulation of ammonia should be the result. The ordinary way to free ammonia would evidently be to raise the alkalinity of the medium as far as possible, but not enough to impede the growth too seriously. . . . The simplest and surest way to obtain this is to let *Azotobacter* bring about this reaction for itself by growing it on silica-jelly impregnated with organic sodium salts, lactate or succinate, but with no other addition than mineral salts. The destruction of acid ions is so rapid in these conditions, that the initial pH of 6.8 — 7.0 rises . . . in two days to 9.0 and above.

Under these conditions by fixing a strip of red litmus paper inside the lid of the Petri dish, or by Nesslerizing water drops condensed on the lid by slow distillation, which can be made more abundant at will, ammonia production can be observed most easily without disturbing the culture. In silica-jelly plates of 20 cm. diameter impregnated with 2 to 2.5 gm. of lactate or succinate, after incubation for 5 days, ammonia accumulates mostly at the rate of 3 mgm. per plate, determined by the aeration method without alkali.

Only material directly isolated from the soil according to the method described in the foregoing was used for the experiments. The cultures were carefully examined under the microscope every day, but neither impurities nor autolyzed cells were found.

These observations were then described in detail by the writer in a paper on the subject published in 1932 (10). However, to keep strictly to the chronological order of publications, a second paper by Kostytchew et al. (4) which appeared in 1931 in the interval between the two papers by the writer will first be reviewed.

The authors evidently knew nothing about the publication of the first of the two, since they do not take any of the data into consideration, nor even mention it. In their new paper, they describe a set of experiments that are intended merely to confirm the results of the first set. But their attitude does not seem quite justified in that a different method is applied and the results are not quite the same.

This time they use the method the writer described in his previous papers (1926-1929), namely, making their cultures in 20 cm. diameter Petri dishes with mannitol silica-jelly. The dishes are inoculated with a strain of *Azotobacter* recently isolated from a soil in the Crimea, and sometimes, apparently, also with earth particles *in natura*. If they do not follow ammonia liberation continuously, they begin analyzing their cultures after a short incubation of 2, 4, and 6 days, consequently using young growth only. Finally, a careful microscopic examination is mentioned.

The quantities of ammonia are found to be as low as a fraction of a milligram for a 2-day-old culture, 1-2 mgm. for a 4- to 6-day-old culture. Nothing is said about finding any amino nitrogen.



So far the results are sound, and the only interpretation is that the ammonia found is due to a process of synthesis: the only possible conclusion where young, active nitrogen-fixing cells are concerned.

Together with this now well-established fact, however, a new observation is announced, namely, that only the ammonia found in young cultures before the carbohydrate is consumed is due to synthesis, whereas ammonia produced by older growth, when the nutrient is already exhausted, is formed by desamination of the cell substance. This view of the question is again suggested by an analogy with molds, where Kostytschew ascribes a double origin to the ammonia found by reduction of nitrate: a primary production by this reduction and a secondary one, which sets in after the disappearance of sugar by desamination of the cell plasma. A similar fact is admitted in the case of *Azotobacter*: primary ammonia—a product of synthesis, secondary ammonia—a degradation product.

It is clear that the only way to prove irrefutably that this desamination process really does take place would be to keep an exact balance of the nitrogen in the cells and in the solution, from which a progressive loss of the former could then be estimated. This too difficult experiment is not attempted by the authors; they merely state that "another mode of ammonia production is not possible in this case." To support this conclusion two sets of experiments are performed: (a) To plate cultures incubated for 8 days and containing appreciable quantities of ammonia a fresh portion of sugar is added: this has the effect of lowering the rate of ammonia and considerably raising the amount of total nitrogen; (b) by growing *Azotobacter* on a dilute solution of peptone and glycol, a considerable amount of ammonia was produced in the absence of mannitol only, whereas the presence of this nutrient had the effect of lowering it to slight traces. Both experiments are supposed to show that *Azotobacter* can really bring about desamination of amines and proteins, which sets in after the destruction of the carbohydrate nutrient.

In the writer's opinion, the aforementioned experiments do not provide a definite proof of desamination, the less so since ammonia liberation by old growth can be explained, at least in part by a different process, which will be discussed hereinafter. The correctness of Kostytschew's assertion is all the more subject to doubt, as this author himself expresses two contradictory opinions on the question: in his first paper he negatives any desamination by *Azotobacter*; in the second, he affirms that the organism is a powerful desamination agent.<sup>3</sup>

The writer's memoir on the synthesis of ammonia by *Azotobacter*, published in March 1932 (10), followed so closely on the second paper by Kostytschew

<sup>3</sup> *Quotations*: First paper "Ausserdem ergab sich dass *Azotobacter* kein desaminierender Organismus ist, da er selbst in Gegenwart von bedeutenden Peptonenmengen keine Ammoniakbildung hervorruft" (3, p. 6). Second paper "Diese Zahlen zeigen, dass auf Peptone allein grosse Mengen von Ammoniak entstanden sind" (4, p. 111) . . . "Sonst wurde dargestellt dass *Azotobacter* ein starkes Desaminierungsgens ist" (4, p. 113).

et al., that the writer, in his turn, could not take it into consideration. This memoir describes extensive studies on ammonia liberation, its condition, and its course.

The fact that ammonia easily accumulates in media where it is blocked by fixed alkali, whereas it mostly fails to be detected in ordinary culture media, seemed to show that free ammonia is in no wise a normal, necessary product accompanying *Azotobacter* growth, but that it may depend on the conditions of growth in general, and on the nutrient offered in particular. A study of the effect of several nutrients of a different kind on ammonia liberation was then planned. Mannitol, glucose, and calcium lactate were tried out under strictly parallel conditions with organic sodium salts, such as lactate, succinate, acetate, butyrate, and propionate. Finally, ethyl alcohol and normal butyl alcohol were used.

It was found that on substances of the first group, which are the better or the best energy materials, ammonia appears late and only in traces; sometimes it is even difficult to detect. Whereas, on poorer nutrients, particularly fatty acids and alcohols, ammonia accumulates more easily, to the extent of some milligrams to a large plate in a few days.

All these observations lead to the general conclusion that the process of nitrogen fixation occurs in two phases, of which ammonia synthesis is the first, and its assimilation, the second, and that these two processes may not always be well balanced. The more active is the growth, the more intense will be the ammonia consumption. On the other hand, every impediment to good growth, whatever its nature may be, whether inferior quality of nutrient, or the lack of it altogether, or any other unfavorable condition, can be supposed to lead to a slowing down of ammonia utilization, which would cause ammonia to be discharged into the medium. Thus it would follow from this assumption that in the soil, where *Azotobacter* can find only inferior nutrients and where the supply is periodically insufficient, the conditions are such as would be particularly favorable to ammonia liberation.

When the writer's results are compared with those in the second paper by Kostytchew et al., it will be noted that the latter obtained ammonia production on mannitol far more easily than did the writer. This difference should not be looked upon as a contradiction, for as the strains used were of a different origin (France and the Crimea), the fixation process for each might well have been regulated differently.

The experimental data are, as already has been remarked, insufficient to decide whether ammonia liberation in old cultures due to desamination, according to Kostytchew, really takes place. But there is another fact that singularly complicates the question. Desamination, as this author insists, is a vital phenomenon (*Lebenserscheinung*) which is suppressed by toluol. The writer's attention was attracted by the fact that *Azotobacter* cells dried and ground up with sand and glycerol, or killed with chloroform, toluol, or ether, continue to

liberate traces of ammonia for a long time. If such is the case, then the idea of a special catalyzer, or synthetic enzyme, which can be isolated from the cells appears to be plausible. This same enzyme may be supposed to function in living cells, be they young or old, producing ammonia, which because of lack of nutrient is no longer drawn off from the old cells into the synthetic process and escapes into the medium.

It is not the writer's purpose here to go into a detailed discussion of this most difficult problem, but only to give a brief critical review of recent investigations, just so far as is necessary in order to outline its present state and to do away with certain misunderstandings.

The writer is inclined to think that his observations of the fixing organisms, where they appear to act as generators and carriers of a synthetic enzyme, will turn the study of the whole problem of biological fixation on a new line that may lead to a clearer understanding of this form of activity.

As a corollary to this review, it emphasizes the fact that the work of Kostytchew et al., and the writer's, executed independently one from the other, though using the same method, lead to an identical conclusion, namely, that the fixation of molecular nitrogen by *Azotobacter* is a reduction process leading to a synthesis of ammonia as a primary product, or one of the primary products of the reaction.

Opposed to this view is a quite different theory, of which Dean Burk is the author. He insists particularly on the fact that all his efforts to detect ammonia in his *Azotobacter* cultures proved unsuccessful (1, p. 1188): "1. Liquid portions of centrifuged cultures were found to contain no nitrogen, by the Kjeldahl method. 2. Alkaline distillations of 10 cc. portions of more than 200 Erlenmeyer flask cultures, grown over a great variety of conditions and ages (up to four months) yielded no trace of ammonia, amines, or other volatile nitrogen bases (less than 0.01 cc. N/100 N, or .0014 mg. of N). 3. Four strains of *Aspergillus niger* molds made no growth when inoculated into cultures of several strains of *Azotobacter chroococcum* regardless of the latter's ages (i.e., up to four months), whereas if traces of fixed nitrogen were given these same mold-inoculated cultures, growth was prominent in less than 24 hours. *Azotobacter chroococcum* cultures of any age, made alkaline with potassium carbonate, could be distilled in steam in a Pregl micro-kjeldahl apparatus for at least half an hour and doubtless longer without yielding volatile bases. 4. More than 200 cultures (as above) were tested by the usual and most sensitive oxygen-nitrogen and oxygen-hydrogen test reagents. . . . with entirely negative results."

The tests, as can be seen, are very careful and numerous. Nevertheless, as a general rule in scientific researches negative facts cannot counterbalance positive ones, when the latter are sufficiently numerous and precise as in the present case. The objection seems then justified, that the student had not had the good fortune to chance on a method suitable to bring out the positive result in question.

Again, it is to be remembered, that a total lack of ammonia production does not contradict the writer's theory, for the balance between production and consumption of ammonia can be constantly at nought. It seems quite possible, that this is the rule with certain strains of this microorganism, especially with stock cultures containing what the writer calls the sugar *Azotobacter*.

There would be nothing more to say about the negative facts already mentioned if Dean Burk's theory about "Azotase and Nitrogenase in *Azotobacter*" (2) were not based on them, i.e., on the non-production of soluble nitrogen as an essential condition. According to this theory, the activity of Azotase, an enzyme system, is normally limited by the extent of growth. Termed *phyto-enzyme*, it is growth bound, that is, correlated with the structure of the living cell to the extent that the velocity of the formation of the (intracellular) reaction product parallels, and is normally limited by, the velocity of growth. The elaborated nitrogen compounds occur in the cell bodies, chiefly as proteins, and are not ordinarily liberated into the culture medium by young and active cultures.

The quotations show how vastly different the fundamental ideas are from which the two theories have sprung. Without going into a criticism of the data of the physicochemical paper (2) where this theory is developed, the writer believes that the facts described in the present paper are in distinct contradiction to the theory about Azotase.

#### THE NITRIFYING ORGANISMS

After the writer's researches on nitrification (1890-1899), numerous careful investigations were made in order to control the data obtained by him. Excepting perhaps some criticisms of details, these data found general confirmation. A review of this collective work is given elsewhere (11). Here it will be sufficient to remark that these studies (1900-1932) were carried out mostly in two directions; namely, isolation of the specific organism in a state of absolute purity—a delicate technical operation, which gave investigators much trouble and was not always successful; and influence of organic matter on their activity. Except by those who worked with a heterogeneous mixture of soil organisms, it was confirmed that the nitrifiers are not able to decompose organic nutrients, but that their growth is even repressed by them, even when present in a very low concentration. Readily assimilating carbonic acid, they appeared as perfect autotrophs. In spite of the repeated confirmation of this characteristic, considerable time was spent in proving them rather to be facultative heterotrophs, but without success.

Whether students were attracted by this question because of its relation to general physiology or more as a consequence of technical difficulties, at any rate, the study of the microbiology of nitrification made little progress where questions of agrobiolgy were principally concerned. The following subjects come under this heading: the isolation and characterization of species or strains from soil samples of different regions; the distribution of the specific organisms

in various habitats (cultivated or uncultivated land, forest soil, swamps, etc.); their adaptation to the conditions of their habitat; the optimum pH for different strains and the influence of the soil pH on their growth in it; methods for determining their density in the soil and the comparison of these densities in soils undergoing diverse treatment, etc. On all these points studies were scarce and were attempted with only indirect methods which could not give clear results.

To open up new possibilities in this domain of research, the writer, with Helen Winogradsky, worked out a new method simplifying the manipulation of the nitrifying bacteria. The method is based on the use of silica-jelly plates *enamelled* with a layer of carbonate of lime, of carbonate of magnesia, or of powdered kaolin (the latter for nitrate organisms). The plates are sprinkled with soil particles; colonies, sprung up round these particles, are reinoculated repeatedly on the same media. Perfectly uniform growth can thus be obtained in a relatively short time, a fortnight or so, quite, or nearly, free from all impurities detectable by careful microscopic examination. Such a state of microscopic homogeneity is quite sufficient for both morphological and agrobiological study of soil nitrification. The culturally controlled purity, which is obligatory in general microbiology and which takes so much time and labor, can be dispensed with. The most important condition for success is a careful exclusion of organic compounds.

Besides being far more efficient than the old, the new method commands better means for dissociating and differentiating strains, for the detection of new species (*Nitrosospira*), and for direct counts of nitrite organisms in the soil, all of which were almost impossible by the old method. The writer hopes that agrobiological studies on nitrification will be greatly facilitated by it.

#### REFERENCES

- (1) BURK, DEAN 1930 The influence of nitrogen gas on the organic catalysis of nitrogen fixation by *Azotobacter*. *Jour. Phys. Chem.* 34: 1174-1194.
- (2) BURK, DEAN 1934 Azotase und Nitrogenase in *Azotobacter*. *Ergebnisse der Enzymforschung*. (Nord und Weidenhagen) 3: 23-56.
- (3) KOSTYTSCHEW, S., RYSKALTSCHUK, A., AND SCHWEZOWA, O. 1926 Biochemische Untersuchungen über *Azotobacter agile*. *Hoppe-Seyler's Ztschr. Physiol. Chem.* 154: 1-17.
- (4) KOSTYTSCHEW, S., AND SCHELOUMOW, A. 1931 Die Stickstoffbindung und Ammoniakproduktion durch *Azotobacter*. *Ztschr. Physiol. Chem.* 198: 105.
- (5) WINOGRADSKY, S. 1925 Etudes sur la microbiologie du sol. I. Sur la méthode. *Ann. Inst. Pasteur* 39: 299-354.
- (6) WINOGRADSKY, S. 1926 Etudes sur la microbiologie du sol. II. Sur les microbes fixateurs d'azote. *Ann. Inst. Pasteur* 40: 455-520.
- (7) WINOGRADSKY, S. 1928 Etudes sur la microbiologie du sol. III. Sur le pouvoir fixateur des terres. *Ann. Inst. Pasteur* 42: 36.
- (8) WINOGRADSKY, S. 1930 Sur la synthèse de l'ammoniac par les *Azotobacter* du sol. *Compt. Rend. Acad. Sci. [Paris]* 190: 661-665.
- (9) WINOGRADSKY, S. 1932 Etudes sur la microbiologie du sol. V. Analyse microbiologique du sol. Principes d'une nouvelle méthode. *Ann. Inst. Pasteur*. 48: 89.

- (10) WINOGRADSKY, S. 1932 Etudes sur la microbiologie du sol. VI. Sur la synthèse de l'ammoniac par les *Azotobacter* du sol. *Ann. Inst. Pasteur* 48: 269.
- (11) WINOGRADSKY, S., AND WINOGRADSKY, HÉLÈNE 1933 Etudes sur la microbiologie du sol. VII. Nouvelles recherches sur les organismes de la nitrification. *Ann. Inst. Pasteur* 50: 350-434.
- (12) ZIEMIECKA, JADWIGA 1932 The *Azotobacter* test of soil fertility applied to the classical fields at Rothamsted. *Jour. Agr. Sci.* 22 (Part 4): 797-810.

## DEVELOPMENT OF SOIL SCIENCE

ALEXIUS A. J. DE'SIGMOND

*Budapest, Hungary*

Soil science today is an independent natural science, but this still young science traveled far before reaching its present stage of development. The history of its evolution includes four main periods: (1) Soil knowledge under the influence of the old philosophy; (2) agronomy in the service of agricultural practice; (3) pedology as a branch of geology; and (4) soil science as an independent science.

### THE FIRST PERIOD

It was inevitable that soil as a medium for plant growth should have been an object of man's interest even during earliest times; during this period, much practical experience and knowledge were transferred from father to son through many centuries. The first recorded theories of the nature of soil were formulated by the Greek philosophers Empedocles (440 B.C.), Aristotle (384–322 B.C.), and Theophrastus (373–228 B.C.). According to their theories, material earth was one of the four elements; furthermore, it was supposed that there existed in the soil some fatty material, which the Latin language expressed by "*oleum unctuosum*." As we shall see, ideas concerning this oily soil constituent, which was later called "*humus*," can be traced up to the eighteenth century. Columella (in the first century) in his book, entitled "*De re rustica*," grouped soils according to their appearance. In the "*Georgics*" of Virgil there is special reference to the oily black soils as one of the many soils mentioned having different colors. But all of these classifications of the ancients were based entirely upon external observations, and were almost entirely lacking in real knowledge of the nature of the soil.

### THE SECOND PERIOD

The first treatise on agronomy to have some foundations upon scientific experimentation was the "*Agriculturae fundamenta chimica*" by I. G. Wallerius (1709–1785) of the Academy of Upsala. Although this contains only traces of real agricultural chemistry, still it was the first report in the history of agronomy to differentiate between humification and peat formation; to describe some physical properties of clay, sandy, and calcareous soils; and to emphasize the importance of soil research. This initial research was continued by Wallerius' successor, the well-known chemist and mineralogist, T. O. Bergmann (1735–1784), who tested soils chemically, and concluded that in the best soil the ratio of clay:sand:lime:soapstone is approximately 4:3:2:1.

Not only chemists, but botanists as well, were interested in soil classification. It is noteworthy that the great botanist, Linnaeus (1707-1778), classified soils according to their natural vegetation and his nomenclature was adopted widely. In this sense, the same man who founded an ingenious system of plant classification, first detected the close relationship between soil types and natural vegetation. Although very acceptable, the soil system of Linnaeus did not yield any profound knowledge of the different soils, because the chemical experiments with soils at that time were still deficient.

It is characteristic of the status of agronomy in the eighteenth century that the Scotch physician Francis Home (1756-1832), in his treatise on "Principles of Agriculture and Plant Growth," approximately 2,000 years after Theophrastus, still attributed to the "oil" of soil an important rôle, especially in the coherence of loamy and clay soils. Though this book is rich in interesting and careful observations on the crummy structure of soil, the coherence of loam, the water capacity of soil, and the formation of saltpeter in soil, the explanation of the phenomena is incorrect because it lacks any chemical or physical basis.

The Frenchman, I. A. Cl. Chaptal, in his book on agricultural chemistry, written in 1823, treated mainly the physical properties of soil, and the several soil analyses that he made were rather inadequate.

The real basis of agricultural chemistry is found in the works of de Saussure, Davy, Thaer, and Einhof. Though the humus theories of Thaer, of de Saussure, and of others were proved unsound by the clear arguments and experiments of Liebig and his successors, nevertheless the aforementioned scientists contributed much chemical knowledge to soil science. This is especially true of the work of Sir Humphry Davy, who, in his book "Elements of Agricultural Chemistry" (London, 1813), pointed out that agricultural plants obtain their food partly from the soil, especially those mineral elements that are relatively deficient in many soils and that, on the other hand, occur in relatively larger quantity in the ash of agricultural plants than in soils.

Thus, soil research was undertaken especially by agricultural chemists, such as Sprengel and Liebig. The former, in his "Bodenkunde oder die Lehre vom Boden" (1837), gathered together all the knowledge of his time and published about 180 chemical soil analyses. Yet Sprengel treated the field of agronomy from a narrow practical viewpoint, studying how far soil research could contribute to plant production. Similarly, the great master of agricultural chemistry, Justus Liebig (1840), though treating the most prominent plant physiological problems of his time clearly and effectively, considered the soil simply as one factor of plant production.

At that time soil physics was also investigated by the agricultural chemist. For example, Gustav Schübler described all of his pioneer work in soil physics in his book on agricultural chemistry, entitled "Grundsätze der Agrikulturchemie in näherer Beziehung auf land- und forstwirtschaftliche Gewerbe" (1831). The same is true of his successors, among whom are found such promi-



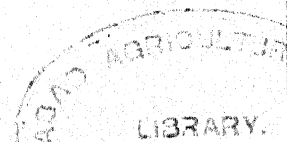
nent scientists as Schumacher, Wollny, King, and investigators in the Bureau of Soils in Washington, D. C., at the time of Milton Whitney. All of these well-known scientific men treated the soil simply as a source of nutrients for plant growth, but not as a natural body worthy of study as such.

There is still another type of investigation in agricultural chemistry which deserves particular mention here. These studies in a field which is partly physical and partly chemical, embrace the phenomenon called "soil absorption." Even as early as 1819, the Italian Gazerri described this phenomenon, and it was investigated later by Bronner, Huxtable, Thompson, Way, Liebig, Mulder, and especially van Bemmelen. The last published his first experiments on soil absorption in 1888 in his papers entitled "*Die Absorptionsverbindungen und das Absorptionsvermögen der Ackererde.*" These publications represent the first steps in colloidal chemistry, the fundamental importance of which in soil science has become so apparent in recent years.

The first traces of still another branch of soil science are encountered during this period of advance in agricultural chemistry. As is well known, the great master of microbiology, Louis Pasteur, suggested the important rôle of bacteria in the transformation of organic matter in the soil: without these microorganisms all dead organic matter would accumulate on the surface of the earth, and plant growth would suffer from a deficiency of nutrients in a short time. Some of the first investigations in soil bacteriology were concerned with those organic materials which contain nitrogen. A description of the fundamental researches on nitrification and on nitrogen-fixing bacteria is not within the scope of this paper, but the work of Warington, Winogradsky, Demoussy, Omelianskii, Beijerinck, Hiltner, Remy, Lipman, Stoklasa, Löhnis, Waksman, and others, which has undoubtedly developed the field of soil bacteriology, should be mentioned. However, their investigations were primarily concerned with problems in the field of agricultural production, as were the researches in the other branches of agronomy during this second period of development of soil science.

It is fitting to mention here Müller, Wollny, and Ramann, who have contributed valuable information on the natural formation of humus and have made other studies of benefit to soil science. The names of Mulder, Grandeau, Tacke, Baumann, Gully, and Sven Oden are also encountered in the research on the chemistry of humus.

Although these different branches of soil science developed nearly side by side, but independently of one another, they served a common end—agricultural production. Just as the agricultural chemists conducted their research work in the service of agricultural production, so also the other branches of soil science were devoted to a similar purpose. Therefore, this period of agricultural chemistry may be differentiated from the next period, that of interest in the geological phases of soil science, though research in both fields had been progressing side by side for some time.



## THE THIRD PERIOD

The German geologist, Fallou, was the first to recognize that the soil itself is a natural body worthy of investigation. It was Fallou, himself, however, who introduced soil science to the field of geology. In this connection, the following quotation from his work is of interest: "Können sich doch nicht einmal die Lehrer der Bodenkunde von jener merkantilischen Betrachtungsweise frei machen, denn sie denken sich den Boden nimmer vor allen Nebenbegriffen abstrahiert, sondern immer nur als Acker der seine Rente tragen muss. Es fehlt an einer wissenschaftlichen Bodenkunde die diesen Namen verdient." Still in his "Pedologie oder allgemeine und besondere Bodenkunde" (1862) his soil classification has a strictly geological-petrographic basis. It is to his credit, however, that he delivered soil science from the shackles of practical domination, and established the scientific basis of agrogeology and soil mapping.

He may have had the correct intention, but as a geologist been led to a geological classification of the soils of his own country; since the relatively narrow region he surveyed was close to the forested region, the local geological agencies differentiated the soils from one another. Shortly afterward his compatriot, M. Fesca, in his book "Die agronomische Bodenuntersuchung und Kartierung" (Berlin, 1879) agreed that geological data are not sufficient scientific standards for the desired classification and characterization of soils. Nevertheless, agrogeology was a good medium for the development of soil mapping on a larger scale than had existed previously. During this period, agricultural chemistry, because of its numerous defeats in the field of practical agriculture, gradually lost its dominant position in research in soil science.

During the last two decades of the nineteenth century a new series of experiments was introduced in Germany by Hellriegel, Wagner, Maercker, and others; these were the so-called "pot experiments." The results were particularly instructive and aided practical agriculture where agricultural chemistry had failed. It may be well to mention here the many disappointments that attended the practical use of chemical analyses of soils. In the so-called "golden age" of agricultural chemistry, it was believed that by the use of chemical analysis it would be possible to give more exact recommendations for fertilization, just as analytical procedures had aided in the manufacture of fertilizers. The methods and principles used at that time in soil analysis, however, brought complete failure. The result of this disappointment, combined with the positive indications of the pot experiments, led to the creation of a general opinion that chemical analysis of soils might be instructive for scientific research, but had no use in practical agriculture. This was the general situation at the beginning of the present century. Only a few prominent chemists such as Déhérain, Schlössing-fils, Gerlach, Dyer, Hilgard, and some others, had not given up hope of finding new promising uses for soil chemistry.

In place of chemical analysis, mechanical analysis, which seemed very promising for characterizing soils physically, was adopted more and more in soils laboratories. Results of mechanical analyses combined with the information from geological and petrographic determinations were commonly obtained in soil research, and these served more or less as scientific criteria for soil classification, nomenclature, and mapping. The soil maps of the "Preussische Geologische Landesanstalt" at Berlin in the first decade of this century represent, perhaps, the best of this type of work. As a result of these tendencies, soil mapping and scientific soil research seemed to be heading toward complete incorporation with geology, with that phase which treats of the surface geology of the earth; in this way it would become but one more practical branch of the geological survey.

In the United States, however, soil surveying was principally centralized under the head of the Bureau of Soils of the Department of Agriculture and was organized to consider the entire country. Mechanical composition of the soil served as the basis for physical characterization, but the real geological characteristics were neglected more or less, since no general relationship was found to exist between the geological origin of the soil and its practical behavior. Petrographic and mineralogic analyses were also considered for use in classification, but not with very promising results; both are too complicated for use in surveying soils. A somewhat subjective method of classification was introduced, however—subjective in the sense that the soils described were different soil series or local types, which had local practical characteristics; a single soil could be sometimes identified by the surveyors with other local soils. For surveying and mapping soils locally this was a fairly feasible procedure, and for practical purposes had much merit as a means of directing the farmers in uniform mass production. Each bulletin, published with the soil map, was an agricultural guide which stated how to produce the best crops on the various local soils. Since these reports were closely correlated with experiments on the local soils and with climatic and hydrographic conditions, they should reflect well the general agricultural conditions of the surveyed land. In these respects the soil maps might be expected simply to serve agriculture but to lack scientific value; such, however, is not the case. They indicate in general that neither the geological origin nor the textural composition of the soil is the general factor in these local soil types that determines their agricultural fertility.

There was still another method of soil surveying practiced in Russia. The founder of this agronomic school was Dokuchaiev (1897), who treated soils as a function of various soil forming factors. He and his successors have developed a new system of soil classification, nomenclature, and soil mapping, based principally upon climatic factors and morphological characteristics. Since this research led to the development of an independent soil science, it may be well to delay its treatment until a consideration of the next period of this historical sketch. However, this Russian zonal classification of soils

should not be confused with the climatic zonal rock weathering introduced by Richthofen. The soil classification of Richthofen actually had a geological basis; he treated soils simply as products of rock weathering and not as a function of all soil-forming factors. It is true that by considering climatic zones in rock weathering, Richthofen introduced at the same time another primary soil forming factor. On the other hand, the soil zones in Russia were mainly distributed in large climatic zones running from southwest to northeast. Indeed, the zonal soil classification of Sibirtzev (1895), the first successor of Dokuchaiev, was principally a soil classification based on climate. But if we study the classifications of both Dokuchaiev and Sibirtsev more closely, we may recognize that, besides climatic factors, they also assign to the natural vegetation, to the soil relief, to the age of the soil, to the parent rock, and to other local factors, equally determining importance in the formation of well-defined soil types. Moreover, they have shown not only that different soil types may be formed from the same parent rock under the influence of differences in climate, but that similar soil types have been formed from very different parent rocks in the same climatic soil zones.

Since the fundamental treatises of the Russian scientists were published only in the Russian language, the international scientific literature did not take notice of them. At about the same period (1892-1894), Hilgard published several papers on the effect of climate on soils, based on his own soil studies. His investigations were not only independent of the Russian school, but they treated quite another field of soil science; he endeavored to indicate the great importance of humid and arid climates in determining the chemical composition of soils and subsoils. He also developed an entirely new school for the interpretation of chemical soil analysis. It is not necessary to emphasize here Hilgard's well-known fundamental researches on alkali soils. He was the first to demonstrate experimentally that the climate of arid regions favors the formation of alkali soils. He made such comprehensive investigations of alkali soils that all students who were interested in the subject considered it necessary to consult his numerous papers and his book on "Soils" (1910) in which he gathered together the valuable results of his experiments. Though he had studied sciences in Germany, as a soil scientist he was a self-made man. He was a pioneer in the reclamation of alkali soils through irrigation and by the use of gypsum; he recommended the cultivation of alkali resistant plants and suggested other treatments for the practical utilization of the soils. He was a great master of true soil science, even though the general conception of soil science as an independent science was still in the embryonic stage of development at the time of his death (1916). He personally took part in the organization of the First Commission of Soil Chemistry during the meetings of the Second International Conference of Agrogeology held at Stockholm in 1910. His brilliant correspondence with the president of this commission indicates that he was a serious and creative student of soils to the end of his life. To him belongs much of the credit for the restoration of soil chemistry to its rightful position in agronomy.

## THE FOURTH PERIOD

It is difficult to state the exact time of the creation of an independent soil science. It has been noted previously that, as early as 1862, Fallou mentioned the idea of an independent soil science. Dokuchaiev considered soil as a natural product of the influences of different soil forming factors on soil material; the product was not primarily determined by its geologic origin nor was it to be considered solely on the merits of its agricultural utilization. This conception indicates that to him soil was as much an object of nature as was a mineral, a plant, or an animal. Hilgard demonstrated by numerous analyses that the composition of a soil can differ greatly from that of the parent rock, and that the characteristics of the soil are greatly affected by the climate. The differences in chemical composition of the arid and humid soils were so striking, and the reasons for these differences were so clearly explained by Hilgard, that his theory spread throughout the scientific world of his time.

These facts may suggest that during this period soil science had already received general recognition as an independent natural science. The scientists mentioned, however, were but single guiding stars. It is a characteristic and an interesting historic tale that Ramann narrates in his paper "Über Bodenkunde und angewandte Bodenkunde oder Technologie des Bodens" (1905). Upon an occasion when a professor of mineralogy asked him what was the field of his studies, Ramann answered, "I am busy in the field of soil science." The professor of mineralogy then inquired, "Does such a science exist?" "Well, Sir," answered Ramann, "if soil science does not exist yet, it will be created now." Indeed Ramann's vision proved correct. This master of soil science fully understood the reasons why soil science could not attain independence of the related sciences. He attempted to settle the controversies and disagreements. There was, however, little opportunity to bring the interested parties together until the meetings of the First International Conference of Agrogeology, held at Budapest in 1909.

In accordance with the proposal of the Hungarian agrogeologists, Treitz, Timkó, Gull, and Béla de Inkey, the late director Lóczy invited agrogeologists and other soil experts to an international conference on the occasion of the fortieth anniversary of the Hungarian Geological Institute. The principal reason for holding this meeting was to discuss the various systems of nomenclature, classification, and cartography of soils which were in use at that time. The Hungarian Geological Institute was commencing some pedological soil mapping, and there was some disagreement as to the procedure that should be followed. Part of the members of the institute recommended adoption of the soil mapping system of the Prussian Geological Institute. The aforementioned agrogeologists, however, preferred the system of soil surveying used in Russia and Roumania; this method was still unknown in other parts of Europe. During the meeting, the Russian school was represented by Glinka, and the German school, by Wahnschaffe; Ramann served as mediator. Glinka fully developed his point of view and stated in conclusion that agrogeology, or pedology, is the science of the soil; that this science is independent of other

sciences or practical considerations; and that soil nomenclature, classification, and soil mapping should be based entirely upon soil genetics. On the other hand, the partisans of the German school emphasized the practical value of the system used by the Prussian Geological Institute. Seven nations (Germany, Austria, Belgium, Hungary, Italy, Norway, and Russia) were represented by the 88 delegates who attended this first international meeting; two other nations (Sweden and the United States) were also represented through reports which appeared on the program of the conference. Although not all of the points of disagreement could be settled during the meeting, the conference was so successful that it was unanimously decided to assemble again the following year in Stockholm at the occasion of the meetings of the Eleventh International Congress of Geology. The group met, however, not as a section of this congress, but separately as the Second International Conference of Agrogeology. Thus started the general movement to deliberate soil science independently of other sciences and considerations. At Stockholm the scientific discussions were well developed, but it became apparent that some permanent organization should be created. The three following permanent commissions were therefore formed: (1) For study of the mechanical analysis of soils. (2) For study of chemical analysis. (3) For consideration of nomenclature for the soil types of the morainic country of northeastern Europe. These commissions fostered the exchange of ideas, and this service was further extended through the medium of the *Internationale Mitteilungen für Bodenkunde*—a journal founded as the official periodical of the International Conference of Agrogeology. This was published, first, under the editorship of Professor Wahnschaffe and, after his death, under that of Professor Schucht. At about the same time two other journals for scientific reports on soils appeared. One of these was the Russian periodical *Pedology*, in which it was possible to publish articles in languages other than Russian. The second was *Soil Science*, established by Doctor Lipman in America in 1916. Both the German and the American periodicals were continued during the World War and these represented the sole connecting links between the soil scientists for the period. After the war, the three commissions and the three periodicals were the international centers from which the movement for the advancement of soil science was revived. Even at the Third International Conference held in Prague in 1922, there was evidence of great interest. The Fourth International Conference in Rome (1924) had such a large attendance and included so many papers and reports that it appeared similar to a congress. At the instigation of Doctor Hissink, the International Society of Soil Science was established during the meetings in Rome; this has continued to be the official organization for the promotion of soil science.

At Rome another important step was taken in the expansion of this international scientific movement. Doctor Lipman was authorized to prepare for the first meeting of the new society, and he invited the members of the Fourth Conference to attend the First International Congress of Soil Science, which

was held in Washington, D. C., in 1927. The President of the United States extended invitations to the foreign governments to be represented by delegates at this congress.

Many far-reaching results and benefits were derived from the meeting: (1) A large number of American scientists became interested in the society, whereas previously few had participated in the conferences of agrogeology. (2) The delegation of 20 soil experts from Russia had the opportunity to develop in detail the results of the modern Russian school of soil science. (3) Membership in the society reached the unprecedented number of 934. Among the members were scientists from all parts of the world where soil science was receiving consideration.

It is impossible to sketch here, even briefly, the numerous interesting reports and lectures which were presented during the ten days of the Congress. Each of the six commissions and some subcommissions into which the society was now divided, held separate sessions. The organization of these divisions at the time of the Congress was as follows:

1. First Commission: soil physics. President Novák, Czechoslovakia.
2. Second Commission: soil chemistry. President de'Sigmond, Hungary.
3. Third Commission: soil microbiology. President Stoklasa, Czechoslovakia.
4. Fourth Commission: soil fertility. President Mitscherlich, Germany.
5. Fifth Commission: nomenclature, classification, and cartography. President Marbut, United States.
  - a. Subcommission for the soil map of Europe: Chairman Stremme, Danzig.
  - b. Subcommission for alkali soils: Chairman de'Sigmond, Hungary.
6. Sixth Commission: application of agricultural engineering to soil science. President Girsberger, Switzerland.

Leading this illustrious group of soil scientists was the president of the First Congress, Doctor Lipman. Previous to the congress he was well known internationally from his studies in the field of soil microbiology and from his editorship of SOIL SCIENCE. During the congress he was distinguished by his remarkable capacity for organization and by his keen sense of diplomacy.

During the organization of the meeting he was aided by a large committee including Doctors Schreiner, Marbut, McCall, and Waksman. Note should also be made of the services of Doctor Hissink, acting president, and of Doctor Schucht, editor of the official review journal.

Since the time of the First Congress many special conferences of the separate commissions have been held in various parts of the world. In 1930, the Second International Congress met in Leningrad and Moscow. At the present writing, preparations are being made for the Third Congress to convene at Oxford during the summer of 1935. The organization for this Congress is as follows:

- First Commission. President Robinson, England.
- Second Commission. President de'Sigmond, Hungary.
- Third Commission. President Waksman, United States.
- Fourth Commission. President Prianischnikov, U. S. S. R.

Fifth Commission. President Marbut, United States.

Subcommissions for soil mappings: For Europe; Stremme, Germany. For the Mediterranean countries; del Villar, Spain. For North America; Marbut, United States. For South America; Matthei, Chili. For Asia; Polynov, U. S. S. R. For Australia; Prescott, Australia.

a. Subcommission for alkali soils; Chairman de'Sigmond.

b. Subcommission for forest soils.

Sixth Commission. President Fauser, Germany.

a. Subcommission for the peat soils: Chairman Ogg, Scotland.

It is apparent that soil science, which, according to Ramann, did not exist 30 years ago, is now sponsored by a well-organized scientific society, which compares favorably with similar societies organized in other fields of natural science. Soil science has now become an independent science without losing contact with related sciences and practical interests. Today soil is conceived to be a dynamic system differing materially from the more stable rocks and minerals from which it is formed. The pedosphere occupies a zone on the surface of our globe between the lithosphere, or regolith, and the biosphere and atmosphere. Although soil is not a living body, it is the home of millions of living organisms. The soil is the cradle and the tomb of all organic life.<sup>1</sup>

<sup>1</sup> The historical data were compiled from the following publications:

'SIGMOND, E. DE. 1934 *Általános Talajtan* (General Soil Science in the Hungarian language). Budapest.

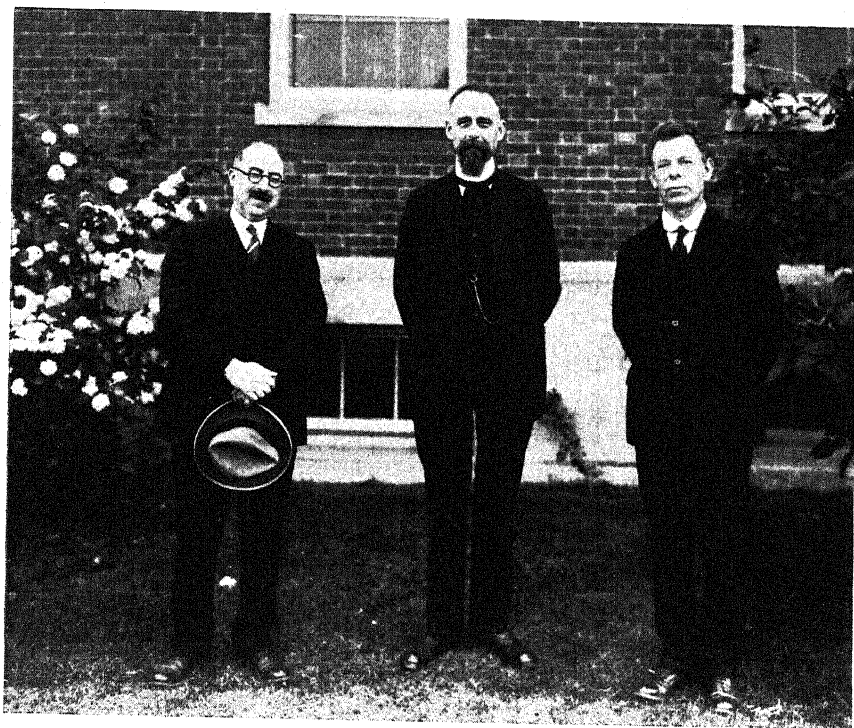
'SIGMOND, A. A. J. DE. 1934 Un court aperçu historique sur les premiers dix ans de l'Association Internationale de la Science du Sol. *Soil Res.* 4: 113-124.

'SIGMOND, A. A. J. DE. 1929 Influence de vingt ans de la coopération internationale sur l'évolution de la science du sol. *Trans. Second Comm. Internatl. Soc. Soil Sci.* (Budapest, Hungary) B: 163-169.

NEUSS, O. 1914 Die Entwicklung der Bodenkunde von ihren ersten Anfängen bis zum Beginn des 20. Jahrhunderts. *Internatl. Mitt. Bodenk.* 4: 453-495.

RAMANN, E. 1913 *Bodenkunde*. J. Springer, Berlin.





DOCTOR LIPMAN AND TWO PROMINENT VISITORS TO THE EXPERIMENT STATION IN 1927



# THE INFLUENCE OF THE SOIL UPON THE GROWTH OF THE PLANT

HENRIK LUNDEGÅRDH

*Experimentalfältet, Stockholm, Sweden*

The growth of the higher plants is determined by a series of influences emanating from the surrounding inorganic nature, which may be divided into climatic, atmospheric, and edafic growth factors. Climatic and atmospheric factors include primarily temperature, light, and precipitation, and edafic factors include, above all, the content and the availability of the nutrient salts in the soil. As is commonly known, it is impossible to draw a definite line between climate and soil factors because the former influences the soil with respect both to type and to the prevailing content of nutrient elements, moisture, and microorganisms. One of the projects in soil science is to determine how the climate affects the formation of certain soil types, irrespective of the influence of geological foundations. The most extensive project and the one most important from a practical standpoint is without doubt the research on the ability of the soil types in question to deliver nutrients to the plants. In this research project are combined physical and analytical chemistry, microbiology, and plant physiology.

The absorption of nutrients by plants and their influence on the growth is a plant physiological problem which may be studied most conveniently with water cultures or pot cultures with moistened quartz sand. In such cultures all the salts may be added in solution, and the influence of the concentration of the various elements may be observed. In the soil, however, there is a series of complicated conditions which primarily depend on the soil's content of organic and inorganic colloids and on the relation of the hydrogen-ion concentration to the solubility of phosphates and carbonates of Ca, Mg, and Fe. A good guide in the application of the results of plant physiological experiments to field conditions is the observation of the *absorption* of nutrients. Formerly the investigator limited himself too closely to looking for a direct relation between plant growth and the absolute amounts of nutrient elements present in, or added to, the soil. It is clear, however, that the physiological effect of one nutrient element depends only on its quantity or concentration within the plant. The rate at which a nutrient element is absorbed is not always in direct proportion to the outer concentration. Ionic antagonism may result in important changes in the relation between outer and inner concentrations. Quantitative ash analyses, therefore, are fundamental to the knowledge of the effect of nutrient elements on growth and yield. For the nitrogen assimilation, moreover, other forms of analysis are necessary.

Thorough investigations by several scientists, among whom Hoagland may be mentioned as one of the earlier ones (7), have shown definitely that elements taken up by the plants through the roots are not absorbed in stable combinations, i.e., as neutral salt molecules, but as anions and cations, whereas the relations between the incoming ions are determined partly by their chemico-physical qualities (charge, volume, etc.) and partly by the energy potential that exists between the protoplasm and the surrounding medium and that is maintained by the life processes, mainly the respiration.

The term "ionic absorption" must not be interpreted to indicate that an anion or a cation enters a cell without the simultaneous release of one equally charged particle from the cell. Such a thing would be impossible, since the ions are strongly electrically charged and any such disturbance of the equilibrium would lead to an immediate discontinuation of the uptake of ions. The concentration of anions remains equal to that of the cations in the nutrient medium, an ion absorption, therefore, always includes an ion exchange between the medium and the living cells. Besides the ion exchange, however, the uptake of undissociated molecules may play a rôle, e.g., in the absorption of  $\text{NH}_4\text{OH}$  at higher pH values (15) or in the uptake of  $\text{SiO}_2$  (9).

If a root system is submerged in a pure solution of, for instance,  $\text{KCl}$ , then as a rule more K ions than Cl ions are taken up while the hydrogen-ion concentration increases correspondingly. In a solution of  $\text{Ca}(\text{NO}_3)_2$  generally more  $\text{NO}_3$  ions than Ca ions are absorbed and the concentration of OH or  $\text{HCO}_3$  ions increases to a corresponding degree. The ion absorption, therefore, simply may be thought of as an exchange of cations for H ions and of anions for OH or  $\text{HCO}_3$  ions between the nutrient medium and the root system. The ion absorption nature of the exchange may be shown in pure salt solutions, where to a certain extent Na, Ca, and K ions are given off from the roots, in exchange for the cations taken up. The varying exchange capacities of Na, K, Rb, Cs, or Ca, Sr, and Ba also are reflected clearly in the different quantities of cations which are forced into the substratum by those previously mentioned (13). Quantitatively, however, the H ions dominate as exchange ions among the cations, since they are produced in unlimited quantities through the respiration processes. The same is true for the anions, OH and  $\text{HCO}_3$ .

That the living cell must develop a certain amount of energy during ion absorption is shown by the fact that salts usually accumulate in the cell in higher concentration than in the surrounding medium. The absorption potential in this case may be looked upon as a lever for the ion absorption, but the potential level must be maintained, which in turn requires energy. It has been shown that a definite relation exists between respiration and the amount of anions absorbed, according to the formula

$$R_t = R_o + k \cdot A,$$

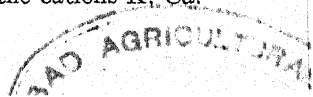
where  $R_t$  = the total respiration,  $R_o$  = the strictly aerobic fundamental respiration ("Grundatmung"), and  $k \cdot A$  = the additional facultatively anaerobic

anion respiration, which is governed by the amount  $A$  of absorbed anions;  $k$  is a coefficient characteristic for each anion (12).

We go further, then, to look at the relation between the concentration of one nutrient element in the substratum and its concentration in the plant. In a pure solution of a nutrient salt the amount of absorbed anions and cations will increase with the outer concentration along a logarithmic curve. If, on the other hand, the solution contains two or more salts simultaneously, usually antagonistic phenomena occur which may change the relation between outer and inner concentration. Ionic antagonism lies in the presence of an ion, e.g., Ca, which will retard the intake of another ion, e.g., K. According to investigations by Burström (1) the extent of the retardation is a function of the interrelation of the concentrations of the two elements affecting each other. It occurs to some degree primarily when the concentrations (in equivalents) of the two elements are about equal and soon reaches its maximum when the concentration of the retarding ion is larger than that of the one being retarded (fig. 1). Burström has found a colloid chemical parallelism to this phenomenon, and thus the theory that ion adsorption and ion exchange form a lever for the salt uptake by the roots is further strengthened. The antagonism K:Ca and Ca:K is of particularly great importance.

Many experiments with water and pot cultures have been performed by plant physiologists and agricultural chemists to determine the importance of nutrient ions to the growth of plants. These experiments have shown, in general, that when one nutrient element is increased with respect to the others an increase in growth occurs which is nearly proportional to the increase in the concentration at the minimum levels but which becomes relatively smaller with higher additions. In the case of very high additions, a decrease in growth has often been established. A number of German workers, Mitscherlich (16) among others, have attempted to trace the growth curves by means of mathematical formulas. The value of such formulas, however, at least from a practical standpoint, is diminished by the fact—as has been shown by Rippel (19) and others—that the effect of every nutrient element depends on the quantity of the other elements present at the same time. Rippel found that with a high content of nitrogen in the soil the effect of potassium on the growth is smaller than with a low content of nitrogen. Here again is an interaction between growth factors somewhat similar to ionic antagonism, although in the present case it may be founded on certain metabolic phenomena. As a proof of the particularly complicated relation between the growth factors and the growth it may be mentioned here that Shive in his extensive trials with water cultures has found that most satisfactory growth can be obtained in solutions of varying composition.

In connection with pot cultures in quartz sand carried out in the author's laboratory, complete ash analyses have been made by means of which the growth produced could be correlated with the inner ion concentration and ionic balance. We shall limit ourselves here to a discussion of the cations K, Ca, Mg, and Mn.



The relation between cation content per unit dry weight and growth produced is most obvious for K (fig. 2). The growth increases uniformly with the inner potassium content up to an optimum, above which larger K contents have little effect. No distinctly injurious effect from the surplus of K (up to 2,200 millimols per kilogram dry weight in the leaf tissues of oats) has been observed. For calcium, at low contents the growth increases very fast with increasing inner Ca content. An optimum is obtained at a relatively low Ca content

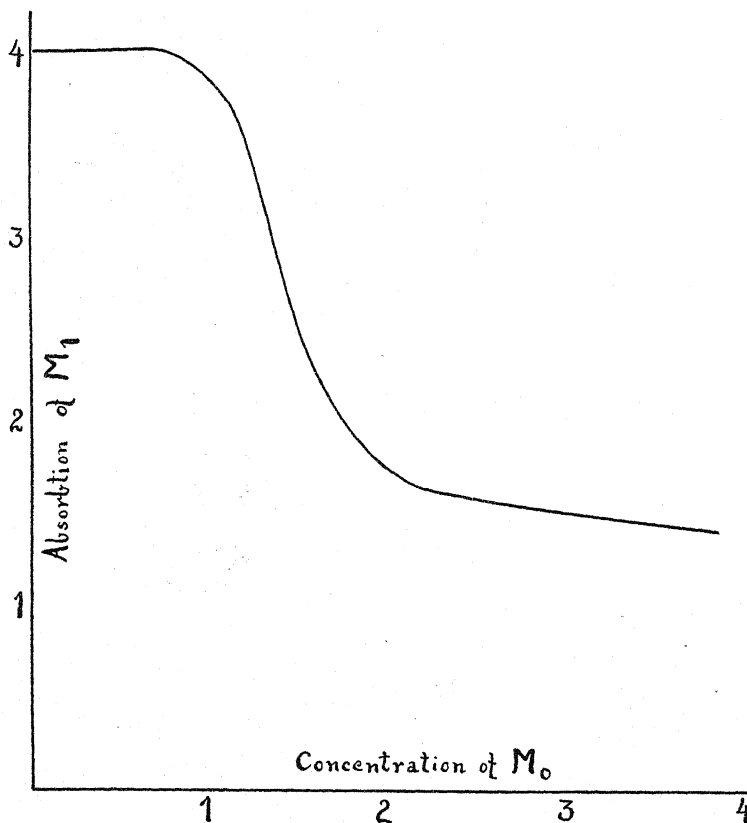


FIG. 1. DIAGRAM OF THE ANTAGONISTIC ACTION OF ONE ION ( $M_0$ ) ON THE ABSORPTION OF A SECOND ION ( $M_1$ )

At the figure 1 on the abscissa the concentrations of  $M_0$  and  $M_1$  are equal.  $M_1$  is constant during the experiments;  $M_0$  is varied. The concentrations are in equivalents (1)

(44 m. mols./kgm.) and only at high Ca contents (above 225 m. mols.) do retarding effects occur. Magnesium acts very similarly, although injurious effects have not necessarily occurred. It appears that exceptionally small amounts (less than 1 m. mol./kgm.) of manganese, which seems to be a necessary nutrient element for oats, produce some effect, but, on the other hand, an injurious effect from a surplus of Mn in the tissues (up to 20 m. mols.) has

not been established. This observation may have some connection with the fact that Mn as well as Fe and to a certain extent also Ca and Mg are bound into insoluble compounds in the tissues.

These briefly related investigations show very clearly the importance of a correct balance between the various ions in the nutrient medium. This fact has already been pointed out by Hansteen-Cranner (5), Osterhout (17), and others, although these workers have not taken into consideration the *inner* ionic balance in the plant, which naturally is the actual cause of the effects on growth. In spite of a medium outer supply of Ca, because of the ion antagonism, a lack of Ca within the plant may occur in the case of an extremely high outer K

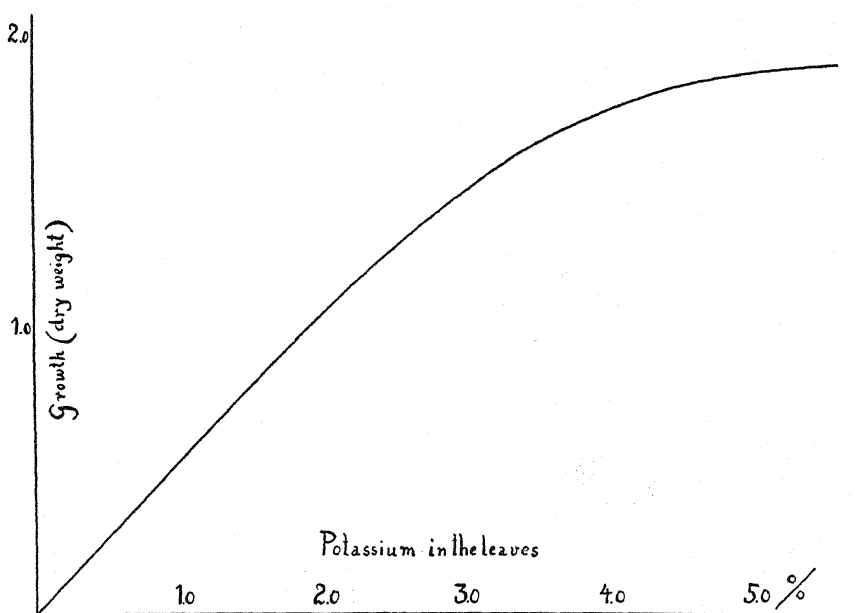


FIG. 2. THE RELATION BETWEEN THE INNER CONCENTRATION OF POTASSIUM IN THE LEAVES OF OATS AND THE GROWTH (9)

concentration. Conversely, at a low outer K concentration even a modest Ca concentration may result in an injurious surplus of this element in the tissues. Similar antagonistic effects in the case of ion absorption occur between K, Mg, and Na and between Ca, Mg, and Mn.  $\text{NH}_4$  also retards the Ca intake (1).

The ion antagonism appears primarily as a surface effect between the medium and the roots and is to be considered as an adsorption substitution of the same kind as the substitutive relations between an inorganic gel with powerful adsorption ability and a solution of neutral salts. The antagonism is strongest between the outermost ions in the adsorption series  $\text{Mn} > \text{Ca} > \text{Mg} > \text{K} > \text{Na}$  (1).

Since, however, the mobility of the ions in a colloidal medium, and thus also

in the plant tissues, is a function of the charge and diameter of the ions, the very mobile K ion will be translocated in the plant much faster than, for instance, the less mobile Ca ion, in which case at an equal outer concentration of these two elements much more potassium will be taken up than calcium. In this case the antagonism *within* the plant of K:Ca will soon dominate. Also the translocation of the ions within the plant is affected by the colloidal chemical character of the protoplasm. Thus potassium to a certain extent favors the translocation of other ions, whereas the presence of calcium retards it (1).

The anions are pulled into the metabolism to a greater extent than are the cations, but a certain luxury absorption, in particular of Cl, might be of importance in facilitating the cation absorption. Here the chemico-physical characters of the anions come into effect. The very mobile  $\text{NO}_3$  ion is a favorable factor for cation absorption; Cl and particularly  $\text{SO}_4$  are less mobile; and  $\text{H}_2\text{PO}_4$  seems to be fairly mobile.

These plant physiological and chemico-physical facts briefly touched upon form the background against which we must look at the problem of the influence of soil on plant growth. As has been mentioned, there is no marked difference between the nutrient uptake from a soil and from a nutrient solution. Certain important differences which present themselves, however, are mentioned in the following.

In the soil the roots of the plants are not freely floating in the soil solution, but the root hairs serving as absorption organs adhere to the humus particles, the clay coagulates, or the colloidal membranes of the mineral particles. Instead of the free and unobstructed supply of ions in a solution we are confronted with a kind of ion transport in a colloidal medium; moreover, the soil colloids mostly have a powerful buffering effect against changes in the reaction. Finally, most of the nutrient substances are not entirely dissolved but are present as adsorption fixations or as chemical compounds, the solubility of which usually is closely related to the hydrogen-ion concentration.

With respect to the direct effect of the soil colloids on the ion absorption, experiments carried out in the author's laboratory, where colloidal humus or  $\text{SiO}_2$  gel has been added to the substratum (ground quartz), have shown that the uptake of the bivalent Ca, Mg and Mn is retarded; this is analogous to the conditions in case of an ion transport within the plant. Probably here also a certain adsorption competition occurs between the colloids of the soil and those of the roots.

Thus, the importance of the buffering effect is clear if we consider that any deviation from the equivalence relation between the cations and anions absorbed is followed by a certain loss of energy by the cells. A one-sided anion absorption (for instance from  $\text{Ca}(\text{NO}_3)_2$ ) may be compensated in a solution to a certain extent with a profuse  $\text{CO}_2$  outgo (11), provided the aeration is not too strong. If, however, the soil is well buffered against an increase in the pH value, this becomes a valuable aid to the anion absorption. Conversely, a



buffering against a lowering of the pH value facilitates a one-sided cation intake. Thus in a well-buffered soil the ion absorption can accommodate itself more readily to the plant's immediate need of the various ions. This is probably one of the explanations of the superiority of the neutral colloidal soils as growing media. To this may be added the large quantities of exchangeable cations which are readily available.

The factors determining the solubility conditions in the soil are of great importance. Thus, for instance, the activity of carbonates and phosphates of Ca, Mg, and Fe and of Mn compounds is very closely related to the actual pH value. Investigations of the solubility of phosphoric acid have been made by Gaarder (4) and others. The following data (9, p. 167) from a pot culture series with lime may serve to illustrate the solubility versus the pH value:

pH value of the pot culture solutions.....	5	6	7
Soluble P in mgm./liter.....	25.1	20.3	12.7
Soluble Ca in mgm./liter.....	848.0	443.0	387.0

In a similar way the solubility of Mg, Fe, and Mn compounds is influenced by the hydrogen-ion concentration. The solubility of Mn, however, increases with an alkaline reaction. With respect to phosphorus compounds it should be pointed out that certain organic esters are available at higher pH values. Mn and Fe take part to a certain extent in the oxidation and reduction processes in the soil.

The importance of the hydrogen-ion concentration to plant growth, however, is not limited to its relation to the solubility of a number of nutrient elements; the speed of absorption bears a definite relation to it also. For chemico-physical reasons the absorption of cations is favored at an alkaline reaction, and that of anions, at an acid reaction. It has been possible to establish this fact in physiological experiments, e.g., with  $\text{NH}_4\text{NO}_3$  (2) or in the case of K and  $\text{H}_2\text{PO}_4$  in the soil (10). Certain trials, however, seem to show that the bivalent elements Ca and Mg act differently, i.e., they are absorbed in greatest amounts at a reaction approaching neutrality (9). These conditions, though as yet insufficiently studied, should be included in a discussion concerning the relation of pH to plant growth. Moreover, it should be pointed out that according to experiments by Prianischnikow, the author, and others (18, 8) the ion antagonism between H ions and Ca ions, which latter thus will counteract the unfavorable influence of higher concentrations of  $\text{H}^+$ , has a definite effect.

In the literature we find analyses representing averages only of the nutrient absorption under natural conditions, whereas the knowledge of the varying influence of the different soil conditions usually is limited to yield data. However, in this case only careful analyses will give information on nutrient substances absorbed in relation to nutrients present in the soil in order to estimate the plant's ability to utilize different soil types. Such parallel analyses of soil and crop have been carried on at the author's laboratory, and so far several

series have been completed, including several hundred cases of oats and sugar beets in Sweden (10). The method employed involves *triple analyses*, made in such way that before the crop reaches maturity samples are taken from the still green leaves, from the soil around the roots, and from the subsoil directly beneath the plant. These samples are later analyzed for K, Na, Ca, Mg, P,

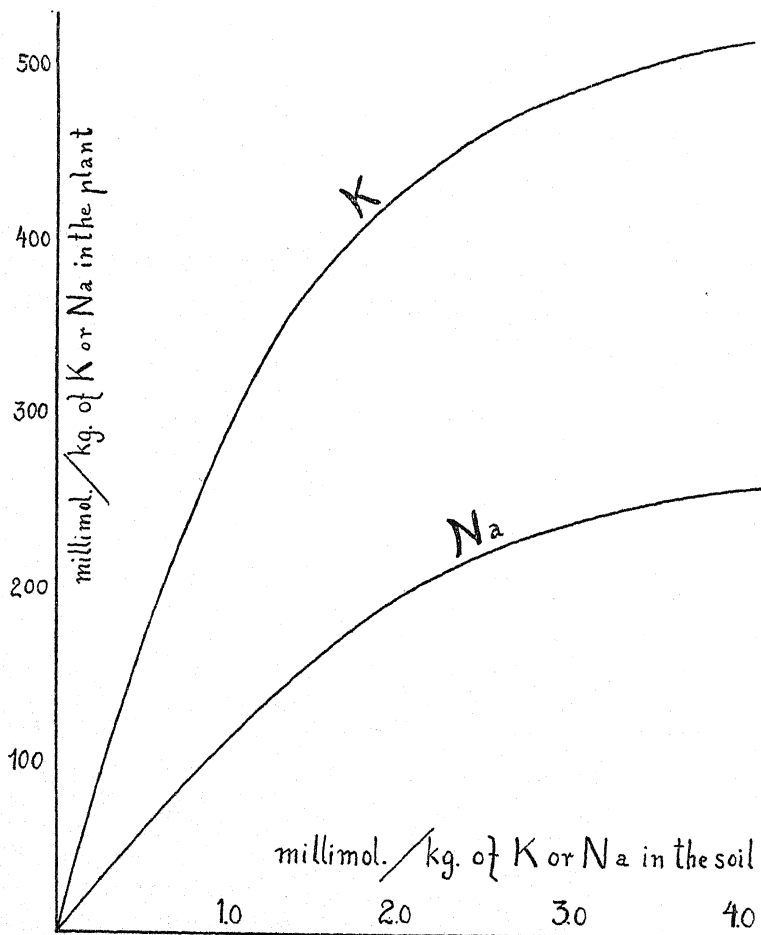


FIG. 3. THE RELATION BETWEEN THE AMOUNT OF AVAILABLE POTASSIUM IN THE SOIL AND ITS CONCENTRATION IN THE PLANT (OATS)

From triple analyses of more than 300 fields in different parts of Sweden (10)

and Mn. The results of the analyses are expressed in millimols per kilogram soil, and per kilogram dry plant matter respectively. A 2-per cent solution of citric acid is used for the soil extracts.

A compilation of analyses of oats with soil analyses in this connection (in this case referring to the surface soil) shows that the alkali content in the

plant increases regularly with the alkali content in the soil, irrespective of the soil type (fig. 3). The absorption of calcium and magnesium at first increases rapidly also with the amount in the soil, but at higher concentrations in the soil an optimum is obtained, and at very high concentrations, conversely, the absorption is somewhat retarded (fig. 4). The manganese absorption is somewhat similar, but the phosphorus intake proved to be rather independent of the content found in the soil extracts. For Ca and Mg, it might be sufficient

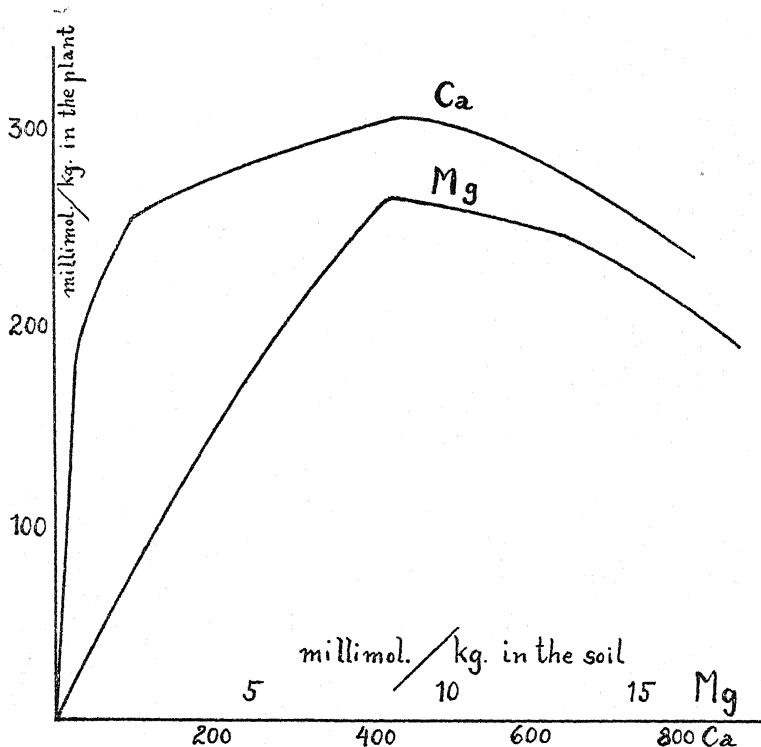


FIG. 4. THE RELATION BETWEEN THE AMOUNT OF CALCIUM AND MAGNESIUM IN THE SOIL (FROM EXTRACTS WITH CITRIC ACID) AND THE CONCENTRATION OF THESE ELEMENTS IN THE PLANT (OATS)

From the same fields as in figure 3 (10)

to refer to the diminishing solubility with increasing contents. The pH value increases regularly with the Ca content, and Ca and Mg as a rule are present in a definite relation to one another in the soil. Also physiologically the absorption of Ca and Mg shows a decrease on the alkaline side. In general, field observations agree well with the theoretical premises.

The quotient  $\frac{V}{S}$  ( $V$  = percentage in vegetation,  $S$  = percentage in soil) expresses the rate of intake for the various elements (table 1). At comparable contents in the soil for the

oats, a series  $K > Na > Mg > Mn$  is obtained, which agrees with results from water cultures.

With increasing content of one element in the soil, naturally the quotient  $\frac{V}{S}$  is lowered. Table 1 includes the average contents of Swedish soils.

The triple analyses bring out also other agreements between the field conditions and the laboratory experiments. Thus there is a definite relation between the calcium content of the soil and the manganese intake, irrespective of the total Mn content (fig. 5). At higher lime content the Mn intake is retarded, and the gray speck disease on grains appears. Investigations by Burström (1) showed that the antagonism of K:Ca appears primarily

TABLE 1

*Values of the quotient  $\frac{V}{S}$  for oats and sugar beets (green leaves) at the normal content of salts in the surface soil*

ELEMENT	K	Ca	Mg	Mn	Na	P
<i>Oats</i>						
Percentage of element in the soil in millimol/kgm.....	1.0	50.0	1.5	0.5	1.0	1.0
Quotient $\frac{V}{S}$ .....	332.0	3.4	35.0	3.5	116.0	114.0
<i>Sugar beets</i>						
Percentage of element in the soil in millimol/kgm.....	1.0	50.0	1.5	0.5	0.5	1.0
Quotient $\frac{V}{S}$ .....	815.0	6.6	271.5	3.8	991.5	

at the equilibrium between K and Ca concentrations. Because of the generally low content of potash in Swedish soils usually no antagonism of K:Ca is noticed. Only in sugar beets, which are known to have a large absorption of alkalies (table 1), can the antagonism be noticed. On soils with low Ca content the antagonism of K:Ca may be easily effected by potash fertilization. Thus it is of importance, in the case of a potash minimum, to supply enough of this material to prevent a calcium surplus in the tissues, from which follows a decrease in growth. For normal development of oats, values of the quotient K:Ca in the leaves of about 1.5–5.0 are required. Too low or too high values are tied up with pathological symptoms. In order to obtain the normal quotient K:Ca the Ca content of the soil should be approximately 50 times greater than the K content.

Recently, with increasing interest, much study has been devoted to those elements in the soil which are present in rather small quantities (Mn, Cu, B, etc.) but which nevertheless have a definite influence on plant growth. The importance of manganese has already been pointed out, i.e., it is indispensable for normal development of oats and beets and of some other cultivated plants. The quantity required, however, is very small (about 0.1 millimol/kgm.). The average content of extractable manganese in Swedish soils is 0.5 milli-

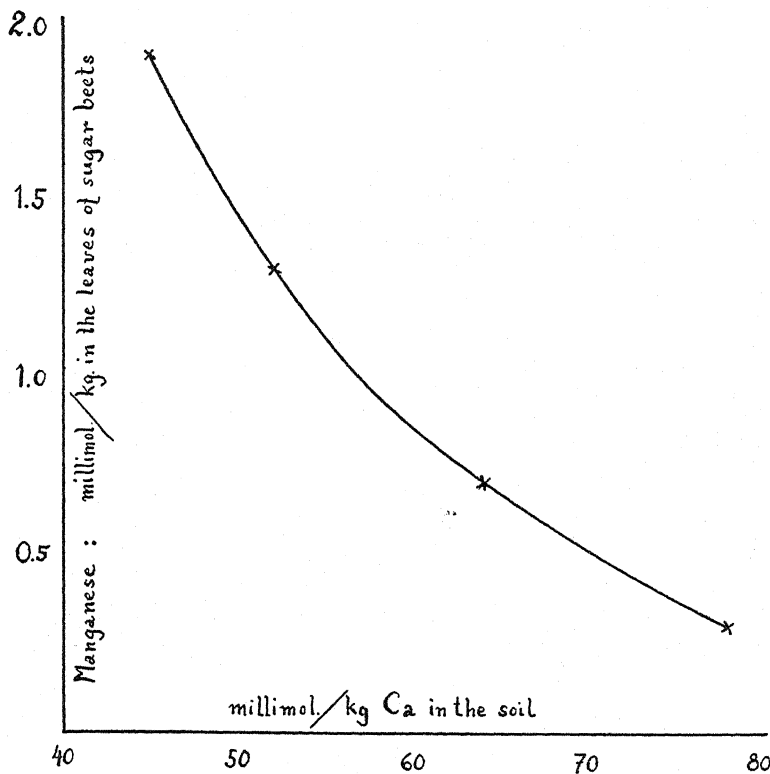


FIG. 5. THE INFLUENCE OF THE CALCIUM CONTENT IN THE SOIL ON THE UPTAKE OF MANGANESE IN SUGAR BEETS

From a field with great variation in the Ca percentage

mol/kgm. but in some individual cases there is a lack of manganese. The unfavorable effect of higher lime content on the manganese intake can be counteracted by the addition of sulfate of ammonia, which will lower the pH value and make the manganese active.

With respect to boron, there are a number of investigations, among which may be mentioned those by Warington (20). The presence of boron seems to favor Ca absorption. This question, however, requires further extensive investigations. The importance and effect of Cu are still less known. Unpublished

data from the author's laboratory show that several metallic ions, such as Cu, Co, Pb, Tl, Hg, have a remarkable effect on the cell mechanism and at even very low concentrations may retard the anion absorption. Very small amounts of, for instance, Cu will stimulate the fundamental respiration. These last mentioned elements, which are active even when present in very small quantities, seem to take part in the enzymatic processes in the protoplasm in a far different way from K, Ca, and Mg and thus very differently affect the progress of growth.

Certain specific influences on the growth may also be derived from organic substances present in the soil or formed through biological processes (3). More recent investigations on auxines seem to point in this direction. In this connection it might be mentioned also that phosphatides given off by the roots normally seem to bear a definite relation to the ion exchange between roots and solution (13). In the soil these phosphatides might influence the microorganisms (14), and it is perhaps not impossible that the thriving of other plants in the same soil may be affected by this work of the roots. These questions, however, are not yet worked out.

#### REFERENCES

- (1) BURSTRÖM, H. 1934 Ueber antagonistische Erscheinungen bei der Kationenaufnahme des Hafers. *Svensk Bot. Tidskr.* 28: 157-263.
- (2) CLARK, H. E., AND SHIVE, J. W. 1934 The influence of the pH of a culture solution on the rates of absorption of ammonium and nitrate nitrogen by the tomato plant. *Soil Sci.* 37: 203-225.
- (3) EULER, H. VON, BURSTRÖM, DAGMAR, AND GÜNTHER, G. 1934 Studien an Phytohormonen. *Svensk Kem. Tidskr.* 46: 250.
- (4) GAARDER, T. 1930 Die Bindung der Phosphorsäure im Erdboden. Westlandets Forstl. Forsökssta. Bergen. Meddel. 14.
- (5) HANSTEEN-CRANNER, B. 1910, 1914 Ueber das Verhalten der Kulturpflanzen zu den Bodensalzen. I-III. *Jahrb. Wiss. Bot.* 47: 289; 53: 536.
- (6) HANSTEEN-CRANNER, B. 1922 Zur Biochemie und Physiologie der Grenzschichten lebender Pflanzenzellen. *Meld. Norges Landbr. Højskole*, vol. 2.
- (7) HOAGLAND, D. R. 1923 The absorption of ions by plants. *Soil Sci.* 16: 225.
- (8) LUNDEGÅRDH, H. 1924 Ueber die Interferenzwirkung von Wasserstoffionen und Neutralsalzionen auf Keimung und Wachstum des Weizens. *Biochem. Ztschr.* 149: 207.
- (9) LUNDEGÅRDH, H. 1932 Die Nährstoffaufnahme der Pflanze. Jena.
- (10) LUNDEGÅRDH, H. 1934 Markbeskaffenhet och gödslingsbehov (Studies in the relations between soil conditions and the absorption of nutrient salts by the plant). Centralanst. Försöksv. Jordbruksområdet [Sweden] Meddel. 444.
- (11) LUNDEGÅRDH, H., AND BURSTRÖM, H. 1933 Atmung und Ionenaufnahme. *Planta* 18: 683.
- (12) LUNDEGÅRDH, H., AND BURSTRÖM, H. 1933 Untersuchungen über die Salzaufnahme der Pflanze. III. Quantitative Beziehungen zwischen Atmung und Anionen-aufnahme. *Biochem. Ztschr.* 261: 235.
- (13) LUNDEGÅRDH, H., BURSTRÖM, H., AND RENNERFELT, E. 1932 Untersuchungen über die Salzaufnahme. II. Die Wirkung der Alkalien und Erdalkalien. *Svensk Bot Tidskr.* 26: 271.
- (14) MELIN, E. 1924 *Svensk. Bot. Tidskr.* 18: 460.

- (15) MEVIUS, W. 1928 *Planta* 6: 379. MEVIUS, W., AND ENGEL, H. 1929 *Planta* 9: 1.
- (16) MITSCHERLICH, A. 1926 Zur Bestimmung des Nährstoffgehalts des Bodens. *Landw. Jahrb.* 64: 191.
- (17) OSTERHOUT, W. J. V. 1914 Various papers on antagonism. *Bot. Gaz.* 58: 178, 272, 367.
- (18) PRIANISCHNIKOW, D. 1923 *Ber. Deut. Bot. Gesell.* 41: 138.
- (19) RIPPPEL, A. 1927 Zur experimentellen Widerlegung des Mitscherlich-Bauleschen Wirkungsgesetzes der Wachstumsfaktoren. *Ztschr. Pflanzenernähr., Düngung, u. Bodenk.* (A) 8: 65.
- (20) WARINGTON, KATHERINE 1934 Studies in the absorption of calcium from nutrient solutions with special reference to the presence or absence of boron. *Ann. Bot.* 48: 743.





## THE AGRONOMIC IMPORTANCE OF CALCIUM

W. P. KELLEY

*University of California*

Among the elements that are essential to the growth of plants, nitrogen, phosphorus, and potassium have long been specially emphasized by agronomists. Soil fertility has come to be regarded as chiefly a matter of available nitrogen, phosphate, and potassium. The fertilizer industry and fertilizer practices have been developed largely on this assumption. Although there is no reason to doubt the importance of these three elements, researches in the field of soil science have shown that too little emphasis has been placed on calcium, for we now know that calcium in soils performs several functions that are of the greatest agronomic significance. The importance of calcium may be considered from the standpoint of soil acidity, plant growth, phosphate availability, soil structure, soil formation, alkali soils, and the use of fertilizers. The calcium content of plants, which is influenced to some extent by the supply of available calcium in the soil, also plays certain highly important functions in animal nutrition.

*Calcium in relation to soil acidity.*—Formerly, soil acidity was thought to be due to soluble substances, chiefly organic. We now know that this is only a minor aspect of the question. The acid substances of soils are, for the most part, not soluble in the ordinary sense, rather they are colloidal in nature and they are both organic and inorganic. Non-saline neutral soils are usually approximately calcium saturated, that is, calcium is the dominant exchangeable cation. Under leaching conditions, the calcium becomes replaced by H ions from the surface of the colloidal particles. In consequence, these particles become acid. As the intensity of the replacement of Ca ions by H ions increases, the inorganic colloidal particles tend to become chemically unstable and this leads to two consequences: (a) Silica becomes split off from the inorganic base-exchange substances, with the resulting formation of clay-like substances having a low silica-alumina ratio and reduced base-exchange capacity. (b) Aluminum comes into play as an exchangeable cation. The remedy for soil acidity is lime; this fact, of course, has long been recognized, but the action of lime is not merely that of a neutralizing agent. The application of lime restores calcium to its place on the colloids and this produces significant effects on various properties of the soil.

The inferior growth of legumes, often noted on acid soils, is not necessarily caused exclusively by excessive concentrations of H ions as such, or by soluble aluminum. Inadequacies in the available calcium supply may be equally as important and in certain cases even more potent. Highly acid soils are usually

deficient in available calcium, and this deficiency is not overcome merely by reducing the H-ion concentration of the soil. That calcium is leached out of decomposing rocks and soils in great quantities was pointed out many years ago by F. W. Clarke in his discussions on the composition of the waters of natural streams. It remained for soil scientists, however, to show the agronomic importance of this process.

*The relation of calcium to plant growth.*—As has been indicated, inadequate supply of calcium in acid soils is often an important factor in the growth of legumes. When grown on such soils, those species of legumes that normally absorb relatively much calcium are often found to contain somewhat subnormal amounts of calcium. Certain important microbiological soil processes are also adversely affected by inadequate calcium supply and by soil acidity. For example, both the symbiotic and certain non-symbiotic nitrogen fixing organisms do not function normally in highly acid soils. This in turn becomes reflected in the growth of higher plants. The development of the root system of plants, both leguminous and non-leguminous, may be greatly influenced by the available calcium supply. For example, when the concentration of calcium falls below a critical level the roots of orange trees manifest pronounced abnormalities; in fact, calcium plays a highly important rôle in the growth of the roots and other parts of several species of citrus and other plants. Calcium also affects the growth of plants through its influence on the absorption of other elements. Within certain limits, an inverse relationship has been found between the absorption of calcium and potassium by plants. Calcium affects the toxicity caused by high concentrations of magnesium and sodium probably largely because of its influence on the absorption of these elements. Through its effect on the pH of the soil,  $\text{CaCO}_3$  may so reduce the solubility of iron in the soil as to produce chlorosis in several different species of plants.

The calcium content of plants, which, as has been stated, is influenced by the availability of the calcium in the soil, has an important influence on their nutritive value as animal feeds. For instance, livestockmen have come to recognize that alfalfa from certain localities is more nutritious than that from others. It is highly probable that the calcium content of the alfalfa is at least one factor in such cases. There are, of course, other factors, such as the phosphorus content of the feed. In the development of the bones of animals and the shell of eggs, calcium plays an indispensable and highly important rôle. In the case of growing children and in certain types of human disease, the importance of the calcium content of the food is widely recognized by physicians.

*Calcium in relation to phosphate availability.*—Generally speaking, a high percentage of the phosphorus of calcium-saturated soils is likely to be available. When soluble phosphate is applied to such soils, it becomes absorbed, that is, fixed, but the fixation of the phosphate is not so extreme as to render the applied phosphate entirely unavailable to the roots of growing plants. On

the other hand, the phosphate of calcium-deficient acid soils is often found to be relatively unavailable, even though the total content of phosphate is comparatively high. Moreover, a considerable part of the phosphate that is applied to highly acid soils tends to become so firmly fixed as to be largely unavailable to growing plants. These facts have not been fully explained. It seems probable, however, that the formation of insoluble phosphates of iron or aluminum is a factor in acid soils, whereas in calcium-saturated soils the phosphate tends to combine with calcium, and hence be more available, since the calcium phosphates are more soluble than the phosphates of iron and aluminum.

However, with soils which contain excesses of  $\text{CaCO}_3$  the Arizona investigators have suggested that soluble phosphates tend to become converted into carbonato-apatite, which is relatively unavailable to plants. At any rate, the availability of phosphate is sometimes low in soils which contain excesses of  $\text{CaCO}_3$ .

*Calcium in relation to soil structure.*—The state of granulation or coagulation of the colloids of a soil markedly influences the tilth of the soil. The kind and relative proportions of the different cations that are combined with, or absorbed on the surface of, the colloidal particles, largely determine the state of granulation of the colloids. Calcium-saturated colloids are usually not highly dispersed; rather they tend to form aggregates. The state of aggregation of soil colloids is closely related to the tilth of the soil. Moreover, carbonic, nitric, and sulfuric acids that are formed in soils by the biological decomposition of organic materials combine with  $\text{CaCO}_3$ , if present, or the H ions of these acids replace calcium from the base-exchange materials. The soluble calcium salts thus formed increase the Ca-ion concentration of the soil solution and this in turn influences the porosity of the soil by virtue of the pronounced coagulating power of Ca ions. Thus it follows that calcium performs important functions in soil physics.

*Calcium in relation to soil formation.*—As long as the upper horizons of a soil contain  $\text{CaCO}_3$ , the dominant exchangeable cation of non-saline soil will be calcium. Under this condition pronounced segregation of the particles of the soil, with the consequent development of dense subsoil horizons, does not take place, because Ca-saturated colloids are not highly dispersed, but under the leaching conditions of humid regions,  $\text{CaCO}_3$  is gradually dissolved and leached out of the soil. This is followed by the replacement of calcium by H ions from the colloids with the consequent production of a dispersed condition of the colloids. The result is the gradual development of dense subsoil horizons. The Putnam series of soils affords a good illustration of the results of this process.

In the initial stages in both the podzolization and lateritization processes,  $\text{CaCO}_3$ , when present as a constituent of the parent materials, is first leached out of the soil, followed by the replacement of calcium by H ions from the soil colloids. This tends, as has been stated, to produce a dispersed condition of

the colloidal particles, but as long as the colloids remain calcium saturated, neither true podzolization nor lateritization takes place. Under comparatively cool temperatures, especially when accompanied by forest cover, the dispersed H-clays that are formed become elutriated downward into the subsoil horizons. The result is, the A-horizon of podzols becomes depleted of absorptive materials. The soil is said to be degraded. Under the high temperatures characteristic of lateritization, on the other hand, the H-clays undergo decomposition with the gradual removal of  $\text{SiO}_2$  and the accumulation of sesquioxides in the upper horizons. Thus it follows that calcium is definitely related to certain important soil-forming processes. The importance attached to calcium in soil-forming processes has led Marbut to propose a broad classification of soils on the basis of their content of  $\text{CaCO}_3$ . If the foregoing reasoning is sound, it would seem more logical to place the emphasis on the degree of Ca-saturation of the soil colloids.

*The relation of calcium to alkali soils.*—Just as H ions replace calcium from soil colloids under humid conditions, with the formation of an acid condition in the soil, sodium tends to replace calcium under arid conditions, with the formation of alkaline conditions. Formerly, an excess of soluble salts was considered to be the most important abnormality of alkali soils. We now know, however, that alterations in the colloidal constituents of the soil, brought about by the replacement of calcium by sodium, are also important, and in certain cases even more important than the soluble salts themselves. The replacement of calcium by sodium, incident to the accumulation of a high concentration of sodium salts, leads directly to significant changes in the physical, chemical, and biological conditions of the soil. The sodium-saturated-exchange substances become highly dispersed when leached, and they undergo hydrolysis with the formation of sodium hydroxide. The net result is a condition extremely unfavorable, both physically and chemically, to plant growth. These adverse physical and chemical conditions are not overcome merely by leaching out the excess of soluble salts. Rather, they are intensified, as a result of the increased tendency toward dispersion and hydrolysis that is brought about by the removal of soluble electrolytes.

Just as in the case of acid soil, the remedy for a sodium soil is calcium. Soluble calcium is able to replace the sodium, thus converting the colloids into a state of calcium saturation, which leads at once to biologically favorable physical and chemical conditions in the soil.

Thus soil science has established a fundamental similarity between acid soils and certain important types of alkali soils. In both, the colloids have become impoverished in calcium. In the case of acid soils the calcium, as has been stated, has been replaced by H ions, whereas with alkali soils calcium has been replaced by sodium, but in the treatment of both, the objective should be to restore calcium to its position on the soil colloids. However, in addition to differences in pH and in the replaceable bases, there is another important difference between acid soils and alkali soils, namely, the latter commonly

contain an excess of  $\text{CaCO}_3$ , despite the fact that the colloids are largely saturated with sodium; whereas, acid soils do not contain  $\text{CaCO}_3$ . The practical treatment of alkali soils in which  $\text{CaCO}_3$  is an important constituent should be such as to increase the solubility of the native  $\text{CaCO}_3$ . Researches in the field of soil science have shown that the oxidation products of elemental sulfur and of organic matter in general, can be caused to accomplish this end.

When a Na-saturated soil is subjected to prolonged weathering under leaching conditions, the colloids, being highly dispersed, undergo translocation downward, thus producing dense sub-soil horizons. According to Gedroiz, the colloidal aluminosilicates may also sustain pronounced decomposition under these conditions. Therefore, the base-exchange materials of the soil are not only removed from the upper horizons of the soil, but also become more or less decomposed. In a word, the evolution of an alkali soil may entail its degradation, somewhat like that of podzolization. However, this degradation of an alkali soil can take place only if the soil is practically free from  $\text{CaCO}_3$ , since, in the presence of  $\text{CaCO}_3$ , Ca ions will replace sodium from the colloids with the consequent formation of flocculated and chemically stable Ca-saturated colloids. Likewise, podzolization does not take place in the presence of  $\text{CaCO}_3$ .

*Calcium in relation to base-exchange capacity.*—Soil scientists hold generally that the base-exchange capacity of a soil is one of its fundamental characteristics. Broadly speaking, base-exchange capacity is a function of two variables, namely, the quantity of certain types of substances present and the kind of such substances. The quantity of inorganic base-exchange substance in a given soil is probably more or less independent of calcium, being largely determined by the content of clay, but its quality appears to be related to calcium. For example, several lines of research have shown that the kinds of clays prevailing in different types of soils differ substantially. Clays related to beidellite appear to predominate in the chernozems and related soil types, and also in immature types of soil such as Yolo, whereas kaolinitic or halloysitic clays seem to predominate in highly weathered soils such as the Cecil and Redding. This is probably true whether the clay has been formed from granitic or basic rocks. Unpublished researches in the writer's laboratory support this view.

It seems probable that the clay minerals that are formed in the comparatively early stages in the weathering of igneous rocks are related to beidellite or montmorillonite. The dominant exchangeable cations of these clays are calcium and magnesium; their base-exchange capacity is relatively high. On the other hand, when these clays, or the soils in which they occur, undergo prolonged weathering, H ions replace calcium and magnesium from the surfaces of the clay particles. The H-clays thus formed are less stable, chemically, than the Ca-forms. In consequence,  $\text{SiO}_2$  gradually splits off, with the resulting formation of clays resembling halloysite or kaolinite, both of which have low base-exchange capacity.

Ca-saturated clays of high silica content are more stable than H-clays, not only chemically, but physically also. The relatively high dispersability of H-clay promotes its elutriation down into the subsoils by natural precipitation. Therefore, the removal of calcium from the colloids may result in the ultimate lowering of the base-exchange capacity of the soil. Obviously, then, if the foregoing reasoning is sound, the maintenance of high base-exchange capacity in a given soil is conditioned upon its colloids remaining in a state of Ca-saturation. If so, the important areas of soils that are now approximately Ca-saturated should be so managed as to preserve a high degree of Ca-saturation.

*Calcium in relation to the use of fertilizers.*—Finally, the calcium content of a soil, especially as regards  $\text{CaCO}_3$  and the base-exchange substances, has a direct bearing on the kind of nitrogenous fertilizers that should be applied. The acids formed biologically from ammonium salts tend to produce extremely unfavorable conditions in soils that are low in calcium (for example, Pennsylvania and Rhode Island experiments). But this is not true if the soil contains an abundance of calcium. Ammonium salts are especially applicable where the soil contains significant amounts of  $\text{CaCO}_3$ . It is possible that the solubility of iron and phosphate compounds in calcareous soils may be significantly increased by the application of ammonium salts. However, it is important to bear in mind that the application of ammonium salts of strong acids promotes the loss of calcium from soils generally, and this fact should always be recognized in planning long-time fertilizer experiments or farm practices.

#### SUMMARY

The purpose of this paper is to call attention to the rather unusual rôle played by calcium as regards soil acidity, soil-plant interrelationships, soil formation, soil profile development, and alkali soil reclamation. Although the importance of nitrogen, phosphorus, and potassium in soils is not to be minimized, it appears that, from several points of view, calcium is of still greater fundamental significance. The reasons for this conclusion are as follows:

The low pH of acid soils is generally associated with deficiencies in calcium. The function that is performed by liming acid soils is not merely that of neutralization. Liming introduces calcium into the base-exchange material of acid soil. Calcium tends to become lost to soils by leaching, perhaps to a greater extent than any other important cation.

Calcium performs important nutrient functions in plants.

Calcium exerts important influences on phosphate availability and on the absorption of other elements by plants.

Calcium influences the physical properties of soils to a marked extent.

Calcium is related to, and exerts a potent influence on, soil-forming processes.

In arid regions the replaceable calcium of the soil is often seriously displaced by sodium. Certain important types of alkali soils are deficient in soluble calcium because of their high pH and content of sodium salts. The deflocculated condition of black alkali soils is due largely to the replacement of calcium by sodium. The colloids of such soils are analogous to those of acid soils in that both are deficient in calcium. In the treatment of each, the object should be to restore calcium to the colloids. Alkaline compounds of calcium are needed with acid soils, whereas soluble forms of calcium are most effective with alkali soils.

The maintenance of high base-exchange capacity in soils is dependent upon the maintenance of approximate calcium saturation of the colloids of the soil. The so-called degradation of the soil is preceded by the removal of calcium, followed by the removal of the clay and its decomposition. Decomposition of the clays referred to herein, denotes the formation of clays relatively low in silica and calcium, that is, clays analogous to halloysite or kaolinite. High base-exchange capacity, in so far as the inorganic colloids of the soil are concerned, is a property of clays similar to beidellite and montmorillonite. In the development of mature soil profiles in humid regions the exchangeable calcium becomes replaced by H ions.

The degree of calcium saturation of a soil, together with its content of  $\text{CaCO}_3$ , is important in connection with the use of ammonium salts as fertilizers.





# THE CLAY CONTENT OF THE SOIL AS RELATED TO CLIMATIC FACTORS, PARTICULARLY TEMPERATURE

HANS JENNY

*University of Missouri*<sup>1</sup>

Received for publication July 23, 1934

The study of soil formation on the basis of the functional concept aims to establish numerical relations (laws) between soil properties and soil forming factors with the aid of the equation

$$\text{soil} = f(m, T, v, p, r, t, \dots) \quad (A)$$

which means that a soil depends on moisture ( $m$ ), temperature ( $T$ ), vegetation ( $v$ ), parent material ( $p$ ), topography ( $r$ ), time ( $t$ ), etc.

In the present paper an attempt is made to correlate the average clay content of soils with climatic factors, particularly temperature. In other words the purpose of this study is to ascertain the nature of the function  $f$  in the equation

$$\text{clay} = f(\text{temperature})_{m, v, p, r, t, \dots} \quad (B)$$

where the subscripts indicate that all the major soil forming factors are to be kept constant.

## SELECTION OF REGION

On the basis of equation (B), which requires constant soil forming factors, the selection of the area to be investigated should be guided by the following principles:

Keep parent material constant, e.g., restrict the study to igneous rocks, or loess, or limestone, etc.

Select soils of similar age but preferably not too young.

Select soils which have developed under comparable climatic moisture conditions (for instance, similar precipitation-evaporation ratios).

Control secondary soil forming factors such as vegetation and topography.

Vary temperature as much as possible.

No large district will be found that strictly meets the aforementioned requirements, but fortunately satisfactory approximations exist. In the eastern, humid part of the United States, an extensive region of igneous and

<sup>1</sup> Missouri Agricultural Experiment Station, Journal Series No. 386.

The author is indebted to Professor C. F. Shaw of the University of California for valuable suggestions and criticisms.

metamorphic rocks reaches from Maine to Alabama and comprises a temperature interval of over 12°C. annual temperature. For the last 30 years the area has been studied intensively by the Bureau of Chemistry and Soils, and numerous soils reports, maps, and mechanical analyses of soils have been published (2). These were taken as the basis for the present study. The counties chosen for the investigation of the clay-temperature relationships are shown in figure 1.

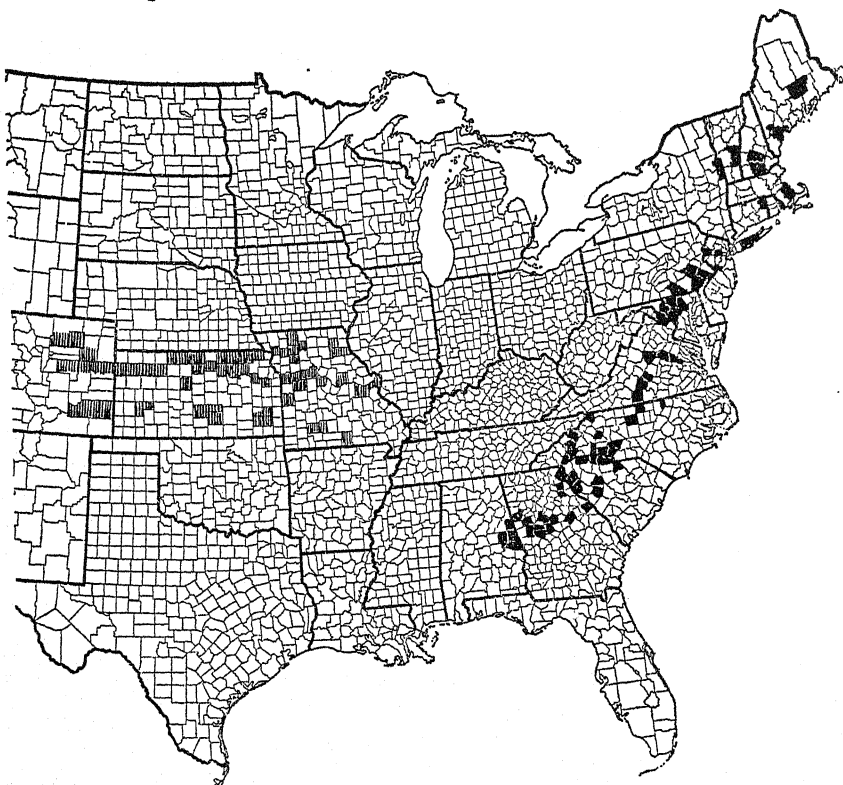


FIG. 1. MAP SHOWING THE LOCATION OF THE COUNTIES OR AREAS INVESTIGATED  
Black areas refer to the clay-temperature study, shaded areas to the clay-rainfall series (5)

#### DESCRIPTION OF METHOD EMPLOYED

At least a thousand mechanical analyses of soils from the district chosen are to be found in the literature, but of these only 151 could be used in accordance with the requirements outlined. The analysis of the data was based upon the following considerations:

In order to avoid soils of mere local occurrence, only those types were included which cover more than 10 per cent of a county area. An exception was made in the case of basic rocks and gneisses in order to obtain enough figures to permit statistical treatment.

Only well-drained upland soils, originally timbered, were assembled.

The crystalline rocks were separated into the following groups: (a) granites, (b) gneisses, (c) schists, (d) basic rocks (gabbro, diorite). In a number of cases the exact nature of these groups could not be ascertained because the soil reports characterize the parent material only as "mixtures of granites and gneisses" or "mixtures of gneisses and schists," etc. Hence, the following additional groups were included: (e) granites and gneisses, (f) gneisses and

TABLE 1  
Data for the parent material group (a) "granites"  
Numbers 1-3 glacial soils; climatic data represent annual values

NUMBER	STATE	COUNTY OR AREA	TEMPERATURE °C.	RAINFALL inches	N.S.C.	SOIL TYPE	CLAY CONTENT per cent
1	New Hampshire	Nashua	7.3	38.8	600	Gloucester stony loam	6.8
2	New Hampshire	Nashua	7.3	38.8	600	Gloucester stony sandy loam	16.8
3	Maine	Cumberland	7.9	42.2	520	Gloucester sandy loam	8.1
4	North Carolina	Mt. Mitchell	12.0	52.5	400	Porters sand	14.5
5	Virginia	Albemarle	12.7	36.9	500	Porters sand	13.5
6	Virginia	Albemarle	12.7	36.9	500	Cecil sandy loam	34.4
7	North Carolina	Henderson	12.9	62.2	400	Porters sandy loam	28.6
8	North Carolina	Henderson	12.9	62.2	400	Porters sand	10.9
9	North Carolina	Caswell	14.3	46.0	400	Durham coarse sandy loam	31.0
10	North Carolina	Cleveland	15.3	53.1	400	Cecil sandy clay loam	48.1
11	South Carolina	Oconee	15.6	53.6	380	Cecil fine sandy loam	25.0
12	South Carolina	Oconee	15.6	53.6	380	Porters fine sandy loam	18.6
13	South Carolina	Cherokee	15.7	48.6	350	Cecil sandy loam	41.4
14	South Carolina	Cherokee	15.7	48.6	350	Cecil sand	24.0
15	South Carolina	Abbeville	16.3	47.6	300	Cecil sandy loam	33.1
16	South Carolina	Lancaster	16.5	44.1	350	Cecil gravelly loam	24.6
17	South Carolina	York	16.8	49.8	300	Cecil fine sandy loam	40.2
18	South Carolina	York	16.8	49.8	300	Cecil sand	39.7
19	Alabama	Chambers	17.2	50.9	300	Cecil clay loam	31.7

schists, (g) granites, gneisses, and schists. To economize in space, individual data are presented only for the groups (a), (b), (d), and (g). (See tables 1-4.)

The "per cent clay" figures refer to the average clay content of a soil profile from the surface to a depth of 36-40 inches (92-102 cm.), calculated as previously (5) by the formula

$$\text{Per cent clay} = \frac{S_1 + 3S_2}{4} \quad (C)$$

where  $S_1$  represents the clay content of the surface soil and  $S_2$  that of the subsoil.

The term "clay" includes all particles having a diameter smaller than  $5\mu$

Climatic data represent annual values

NUMBER	STATE	COUNTY OR AREA	TEMPERATURE	RAINFALL	N.S.Q.	SOIL TYPE	CLAY CONTENT
			°C.	inches			per cent
1	Pennsylvania	Berks	10.7	44.5	340	Chester loam	27.1
2	Pennsylvania	Chester	10.8	49.3	400	Chester loam	22.3
3	Pennsylvania	Chester	10.8	49.3	400	Brandywine loam	18.8
4	North Carolina	Transylvania	12.8	63.7	400	Porters sandy loam	22.7
5	Virginia	Campbell	13.8	41.8	320	Iredell	23.6
6	Virginia	Pittsylvania	14.9	42.1	350	Durham fine sandy loam	18.9
7	South Carolina	Oconee	15.6	53.6	380	Cecil clay	32.8
8	South Carolina	Oconee	15.6	53.6	380	Porters clay	38.8
9	Georgia	Coweta	16.7	50.9	320	Cecil sandy loam	33.1
10	Georgia	Oconee	16.7	48.1	320	Cecil sandy clay loam	36.3
11	South Carolina	Saluda	17.4	47.6	300	Cecil clay	42.5
12	Georgia	Franklin	19.8	50.2	320	Cecil clay	45.5
13	Georgia	Franklin	19.8	50.2	320	Cecil sandy loam	29.1

TABLE 3

Data for the parent material group (d) "basic rocks"

Climatic data represent annual values

NUMBER	STATE	COUNTY OR AREA	TEMPERATURE	RAINFALL	N.S.Q.	SOIL TYPE	CLAY CONTENT
			°C.	inches			per cent
1	New Jersey	Bernardsville	10.0	48.4	400	Montalto silt loam	14.4
2	New Jersey	Belvidere	10.8	47.9	400	Montalto silt loam	13.9
3	New Jersey	Trenton	12.0	48.8	437	Cecil loam	22.3
4	Maryland	Montgomery	12.1	38.4	350	Conowingo silt loam	19.5
5	Virginia	Leesburg	12.2	40.3	450	Iredell clay loam	37.6
6	Maryland	Howard	12.8	42.7	316	Montalto clay loam	29.7
7	Maryland	Howard	12.8	42.7	316	Mecklenburg loam	18.7
8	Maryland	Baltimore	13.0	42.7	316	Mecklenburg loam	17.2
9	Maryland	Baltimore	13.0	42.7	316	Iredell silt loam	19.3
10	Maryland	Baltimore	13.0	42.7	316	Conowingo silt loam	17.7
11	North Carolina	Caswell	14.3	46.0	400	Iredell sandy loam	45.3
12	North Carolina	Cabarrus	15.1	46.9	300	Iredell fine sandy loam	41.6
13	North Carolina	Cabarrus	15.1	46.9	300	Mecklenburg clay loam	45.0
14	North Carolina	Cabarrus	15.1	46.9	300	Mecklenburg sandy loam	35.8
15	North Carolina	Mecklenburg	15.6	46.9	300	Iredell fine sandy loam	32.9
16	North Carolina	Mecklenburg	15.6	46.9	300	Mecklenburg clay loam	41.9
17	North Carolina	Mecklenburg	15.6	46.9	300	Mecklenburg loam	42.7
18	North Carolina	Gaston	15.7	46.9	300	Iredell clay loam	32.6
19	South Carolina	Abbeville	16.3	47.6	300	Iredell clay loam	41.5
20	South Carolina	York	16.8	49.8	300	Iredell clay loam	39.7
21	Georgia	Meriwether	16.8	48.9	300	Davidson clay	51.1

(dispersion with ammonia). Compared with modern technique of mechanical soil analyses the values are consistently somewhat low, but are comparable

TABLE 4  
Data for the parent material group (g) "granites, gneisses, and schists"  
Numbers 1-7 are glacial soils; climatic data represent annual values

NUMBER	STATE	COUNTY OR AREA	TEMPERATURE	RAINFALL	N.S.Q.	SOIL TYPE	CLAY CONTENT
			°C.	inches			per cent
1	Maine	Orono	6.3	42.3	520	Bangor loam	16.0
2	New Hampshire	Nashua	7.3	38.8	600	Gloucester stony loam	6.8
3	New Hampshire	Nashua	7.3	38.8	600	Gloucester stony sandy loam	16.8
4	New Hampshire	Merrimack	7.3	38.8	600	Gloucester stony loam	12.9
5	New Hampshire	Merrimack	7.3	38.8	600	Gloucester stony sandy loam	5.9
6	Connecticut	Windham	8.3	43.9	450	Gloucester stony fine sandy loam	5.5
7	Connecticut	Windham	8.3	43.9	450	Gloucester fine sandy loam	6.2
8	North Carolina	Ashe	8.9	60.2	400	Ashe loam	15.1
9	North Carolina	Ashe	8.9	60.2	400	Porters clay loam	23.9
10	Pennsylvania	Montgomery	11.8	44.9	400	Chester loam	25.3
11	North Carolina	Mt. Mitchell	12.0	52.5	400	Porters clay	30.3
12	North Carolina	Mt. Mitchell	12.0	52.5	400	Porters black loam	22.5
13	North Carolina	Mt. Mitchell	12.0	52.5	400	Porters sandy loam	21.2
14	North Carolina	Henderson	12.9	62.2	400	Porters loam	28.9
15	North Carolina	Caswell	14.3	46.0	400	Cecil sandy loam	34.5
16	North Carolina	Hickory	14.6	49.5	400	Cecil sandy loam	31.3
17	North Carolina	Hickory	14.6	49.5	400	Cecil clay	35.7
18	North Carolina	Hickory	14.6	49.5	400	Porters sandy loam	34.5
19	North Carolina	Mecklenburg	15.6	46.9	300	Cecil clay loam	36.4
20	North Carolina	Mecklenburg	15.6	46.9	300	Cecil sandy loam	34.8
21	North Carolina	Mecklenburg	15.6	46.9	300	Cecil clay	57.5
22	North Carolina	Mecklenburg	15.6	46.9	300	Cecil fine sandy loam	41.5
23	South Carolina	Oconee	15.6	56.7	380	Porters loam	28.9
24	North Carolina	Gaston	15.7	46.9	300	Cecil sandy loam	30.9
25	North Carolina	Gaston	15.7	46.9	300	Cecil coarse sandy loam	43.5
26	South Carolina	Campobello	15.8	44.0	300	Cecil clay	50.0
27	South Carolina	Abbeville	16.3	47.6	300	Cecil clay	40.0
28	South Carolina	York	16.8	50.0	300	Cecil clay	52.5
29	Georgia	Spalding	16.9	44.1	320	Cecil clay	53.3
30	Georgia	Pike	17.2	51.0	300	Cecil sandy loam	37.2
31	Alabama	Lee	18.4	51.0	300	Cecil sandy loam	31.0

among themselves. The fact that the samples were collected and analyzed over a period of 30 years tends to eliminate accumulation of systematic errors.

All data reported in tables 1-4 refer to but single profiles except in a few cases which are averages of two or three samples.

AVERAGE SOIL CLAY LEVELS IN NORTHEASTERN AND SOUTHEASTERN  
UNITED STATES

The average clay contents of the soils of the northern (latitude 35-45°N) and southern parts (latitude 30-35°N) of the region investigated differ remarkably, as shown in table 5. The northern clay level contains 16.3 per cent clay, the southern has a value of 38.0 per cent, a difference amounting to 21.7 per cent  $\pm 1.77$ , which is statistically highly significant. Generally speaking, *the southern soils contain about 2.33 times more clay than the northern ones.*

TABLE 5  
*Clay levels of northern and southern latitudes*  
Depth 0-3 feet

LATITUDE	TEMPERATURE RANGE	GEOGRAPHIC REGION (STATES)	NUMBER OF PROFILES	AVERAGE CLAY CONTENT
	°C.			<i>per cent</i>
35°-45°	6-12	New England States, New York, Pennsylvania, New Jersey, Maryland, North Carolina. (Glaciated and unglaciated region)	39	16.3 $\pm$ 1.18*
30°-35°	16-19	South Carolina, Georgia, Alabama	33	38.0 $\pm$ 1.30

\* Mean error.

THE CAUSES OF THE DIFFERENT CLAY LEVELS IN NORTHERN AND SOUTHERN  
LATITUDES

In table 5 are given the annual temperatures which correspond to the latitudes cited. It is evident that a decided parallelism between temperature intervals and clay levels exists. In spite of such a correlation it is not permissible to conclude that temperature is solely responsible for the observed differences in the clay content of the soils. A number of soil forming factors have not been rigidly controlled, and a glance at the tables 1-4 indicates that such variables as age (glaciation influence) type of igneous rocks, erosion, and fluctuating moisture need careful consideration before the rôle of temperature can be evaluated in a quantitative manner.

*The factor age (influence of glaciation)*

Throughout the Pleistocene the greater part of the Piedmont Plateau has been free from glaciation. The New England States were covered by the last ice sheet, but since the retreat of the ice masses soil formation could have been proceeding for at least ten to twenty thousand years. Indeed, in certain localities mature profiles have been developed (podzols). Furthermore, it is very

likely that the mechanical grinding of the moving glaciers has augmented the clay content of these "glaciated soils," which are derived from ground moraines made up of igneous rock debris. On the other hand, one might contend that glaciation has retarded clay formation and that the low clay levels of northern latitudes are due to the youthfulness of the soils rather than to environmental conditions. From the viewpoint of temperature inquiry it appears desirable to treat the soils of glaciated districts separately in order to avoid uncertainty in the interpretation of the data.

Table 6 shows the clay levels of the unglaciated area only. The differences in the clay contents of the soils for the selected intervals still persist. The northern Piedmont Region differs from the southern by  $12.4 \pm 1.80$  per cent, a value which again is statistically very significant.

*Types of igneous and metamorphic rocks and their effect on clay formation*

All soils which are assembled in tables 5 and 6 have been derived from igneous and metamorphic rocks. It is commonly believed that basic rocks

TABLE 6  
*Clay levels for various latitudes and temperature intervals*  
Glaciated areas excluded

LATITUDE	TEMPERATURE RANGE	GEOGRAPHIC REGION (STATES)	NUMBER OF PROFILES	AVERAGE CLAY CONTENT
	°C.			<i>per cent</i>
35-41°	10-13	Pennsylvania, New Jersey, Maryland, Virginia, North Carolina	38	$25.6 \pm 1.24^*$
30-35°	16-19	South Carolina, Georgia, Alabama	33	$38.0 \pm 1.30$

\* Mean error.

tend to weather faster than gneisses, and if the former are particularly abundant in the South, one would expect a relation exactly like that presented in tables 5 and 6. It becomes necessary to determine the clay levels for each of the separate groups of crystalline rocks, if possible by a series of continuous functions. Such correlations can indeed be observed as indicated by figures 2 and 3, which illustrate the relation between the clay content of the groups (d) and (g) and the latitude, the latter expressed on a temperature scale. The curves, fitted according to the method of least squares, follow the straight line equation:

$$\text{per cent clay} = a_1 T + b_1 \quad (D)$$

where  $T$  represents the average annual temperature in centigrade and  $a_1$ ,  $b_1$  are constants.

Similar relationships hold for the other groups of parent materials as seen from data in table 7, which contains the values of the constants of equation (D) and also the corresponding correlation coefficients. The latter—giving

due consideration to degrees of freedom—are very significant and prove definitely that the clay content of soils derived from uniform parent materials increases in a regular manner from north to south.

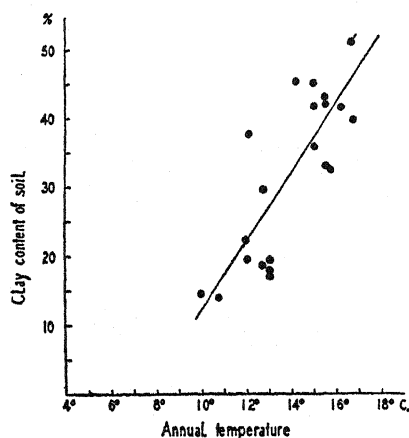


FIG. 2

FIG. 2. GENERAL NORTH-SOUTH CORRELATION BETWEEN CLAY CONTENT OF SOIL AND LATITUDE (ANNUAL TEMPERATURE)

Data refer to parent material group (d) or "basic rocks"

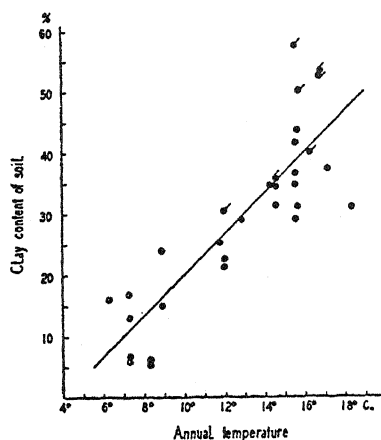


FIG. 3

FIG. 3. GENERAL NORTH-SOUTH CORRELATION BETWEEN CLAY CONTENT OF SOIL AND LATITUDE (ANNUAL TEMPERATURE)

Data refer to parent material group (g) "granites, gneisses, and schists." Semi-black dots indicate soils derived from moraines.

TABLE 7

*General north-south correlations*

Data showing the type of parent material, correlation coefficients, and the values of the constants of equation ( $D$ ).

NUMBER	PARENT MATERIAL	NUMBER OF PROFILES	$a_1$	$b_1$	CORRELATION COEFFICIENT $r$
a	Granites	19	2.64	-10.4	+0.700
b	Gneisses	13	2.02	-0.2	+0.717
c	Schists	22	2.66	-5.3	+0.756
d	Basic rocks	21	4.94	-37.5	+0.814
e	Granites and gneisses	27	3.58	-24.8	+0.707
f	Gneisses and schists	18	2.15	+2.6	+0.490
g	Granites, gneisses, and schists	31	3.33	-13.4	+0.856

### *The rôle of erosion*

On account of specific cropping customs the problem of erosion assumes great magnitudes in the southern part of the region studied. The original soils were Cecil sand and Cecil sandy loam, the porous surface horizons resting



on subsoils of heavy clay. As a result of sheet erosion, much of the original surface soil or A horizon has been stripped away thus giving rise to large areas that are now Cecil clay. Naturally this feature tends to accentuate the higher clay levels in the South.

In figures 2 and 3 all points which represent soils of the clay types (Cecil clay) have been marked by a little dash, and, indeed, many of the higher clay values *appear* to be related to sheet erosion. To test further the quantitative influence of erosion, table 8 containing the data of table 7 split into two groups according to textural differences,<sup>2</sup> has been constructed: first, the heavy-textured soil types (clays and clay loams), which supposedly owe their clayey

TABLE 8

*Data showing that the clay content increases in light-textured as well as in heavy-textured soils*  
Glaciated areas excluded

GROUPS	TEMPERATURE INTERVAL, 10-13°C.		TEMPERATURE INTERVAL, 16-19°C.		IN- CREASE
	Sam- ples	Clay	Sam- ples	Clay	
		<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
Light textures only.....	33	22.0 $\pm$ 1.20	20	32.9 $\pm$ 1.30	50
Heavy textures only.....	7	30.8 $\pm$ 2.33	13	43.4 $\pm$ 1.75	41

TABLE 9

*The clay content of subsoils of light- and heavy-textured soils as related to temperature intervals*  
Glaciated areas excluded

GROUPS	TEMPERATURE INTERVAL, 10-13°C.		TEMPERATURE INTERVAL, 13-19°C.		IN- CREASE
	Sam- ples	Clay	Sam- ples	Clay	
		<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
All textures.....	40	24.8 $\pm$ 1.32	33	44.8 $\pm$ 1.42	81
Light textures only.....	33	23.2 $\pm$ 1.22	20	41.7 $\pm$ 1.65	80
Heavy textures only.....	7	32.8 $\pm$ 2.96	13	49.7 $\pm$ 1.96	52

surface layer to erosion; and, secondly, the light-textured soils, which represent more nearly the original conditions. According to table 8 both groups are characterized by specific clay levels. The most important feature lies in the consistency of the higher clay levels in the South as compared with the North.

The factor erosion can be practically eliminated by restricting the comparisons to the clay content of the subsoil or B-horizon. This has been done in table 9. The latitude effect is even more strikingly manifested than in the profile data of table 8. The subsoil clay levels change from 24.8 per cent to

<sup>2</sup> According to the United States Soil Survey the texture of a soil type is determined upon the mechanical analyses of only the surface soil.

44.8 per cent clay, the increase amounting to over 80 per cent. The difference,  $20.0 \pm 1.95$  per cent, is highly significant. Again the north-south correlation holds for coarse-textured as well as fine-textured soils. Particular significance should be attached to the fact that within each temperature class the heavier soil types tend to have more clay in the subsoil than the lighter types. Apparently the higher clay content of eroded soil profiles (e.g., clays and clay loams of table 8) is not entirely due to the exposure of the subsoil but is primarily a consequence of the inherently higher clay content of the entire profile. It is quite possible that these different values of the two texture groups reflect differences in the degree of maturity of the soils.

The data in tables 8 and 9 strongly suggest that erosion plays but a minor rôle in the clay latitude relationship, and in the following discussions it is considered as negligible.

### *Discussion of the moisture influence*

The seasonal variations of precipitation, which are similar over the entire area, belong to the so-called Eastern Rainfall Type, which is characterized by a comparatively uniform distribution of rainfall throughout the year. In the northern region a fraction (less than one fifth) of the annual precipitation falls as snow, which "affords the water better facilities for soaking into the ground than though the same amount was poured down during the comparatively brief period of a shower" (7).

The average annual rainfall for the temperature class  $10-13^{\circ}\text{C}$ . is  $48.0 \pm 1.35$  inches, and the corresponding value for the  $16-19^{\circ}\text{C}$ . class is  $48.9 \pm 0.43$  inches. Inasmuch, as this difference is insignificant one might be tempted to consider the graphs of figures 2 and 3 and the data in tables 6-9 as the clay temperature functions searched for. Such a procedure can not be correct because it neglects the rôle of temperature in increasing transpiration and evaporation. Crowther (3) has shown that under conditions of Rothamsted lysimeters, temperature markedly influences the amount of water percolating through the soil. To maintain constant drainage a temperature rise of  $1^{\circ}\text{F}$ . must be accompanied by 0.75 inches more rain. When Crowther's leaching factor was calculated for all counties, satisfactory clay-temperature relations were obtained. However, for the sake of comparison with previous work and with studies on other continents the N.S. Quotient, which is closely related to the precipitation-evaporation ratio, was chosen as the moisture criterion (4).

### *The clay moisture function*

According to the data in table 4, there exists between moisture values and temperature a negative correlation, which can be expressed mathematically as

$$\text{N.S.Q.} = -20.6 T + 6.55 \quad (r = -0.680) \quad (E)$$

$$\text{Leaching factor} = -1.03 T + 53.0 \quad (r = -0.534) \quad (F)$$

These correlations state that with increasing temperature the effective moisture values become smaller. On the basis of the selected moisture criteria there is actually less effective moisture in the South than in the North and the specific rôle of temperature is overshadowed. To discover the true influence of temperature, evaluation of the clay-moisture functions is required.

In a previous publication (5) it was demonstrated that, for soils from homogeneous as well as heterogeneous parent materials, at a constant temperature of 12°C. (11.1–13.3°), the clay content of the soil varies with N.S.Q. as follows:

$$\text{per cent clay} = m (\text{N.S.Q.}) + n \quad (G)$$

where  $m$  and  $n$  are constants. Equation (G) can be applied with little difficulty to crystalline rocks. For instance, for the series "granite, gneiss, and schists," the average clay content at 12°C. (11.1–13.3°) is 25.6 per cent and N.S.Q. is 400 (table 4). The ratio 25.6:400 yields the constant  $m$  in equation (G). For crystalline rocks in general the constant  $n$  can be taken as zero, hence

$$\text{per cent clay} = 0.064 \text{ N.S.Q.}_{(T=12)} \quad (H)$$

which represents the clay-moisture relation for the parent material group (g).

#### *The final clay-temperature functions*

It is reasonable to assume that equation (G) is not only valid at 12°C. but also at other temperatures, and on this basis it is possible to calculate the clay levels for any desired N.S.Q. value. In order to remain within the humid region all data have been adjusted to N.S.Q. = 400 by use of the equation:

$$\text{Per cent clay}_{400} = \text{clay}_{\text{N.S.Q.}} \times \frac{400}{\text{N.S.Q.}} \quad (I)$$

where  $\text{clay}_{\text{N.S.Q.}}$  and N.S.Q. are the observed corresponding values in tables 1–4. Several typical curves are shown in figures 4–7 and the data can all be represented by the general equation:

$$\text{Log}_{10} \text{ per cent clay} = aT_{10}^{200} + b, \text{ or,} \quad (J)$$

after transformation to natural logarithms,

$$\text{per cent clay} = Ce^{kT_{10}^{200}} \quad (K)$$

Table 10 contains the values of the constants  $a$  and  $b$ , and also the correlation coefficients of equation (J) for all groups of parent materials investigated. Since all correlations are significant, the conclusions follow that the *clay content of comparable soils increases exponentially with increasing temperature.*

Many other equations might fit the data equally well as, if not better than, equation (J). It is simply claimed that equation (J) is able to describe the

relationships significantly as judged by statistical criteria. The reason for avoiding straight line functions, as might be suggested by figures 5 and 6, is

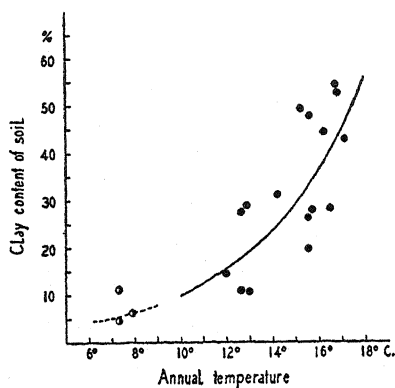


FIG. 4. CLAY-TEMPERATURE FUNCTION FOR THE PARENT MATERIAL GROUP (a) "GRANITES"

Data adjusted to constant N.S.Q. 400. Semi-black points refer to glaciated regions, e.g., soils developed on granitic moraines.

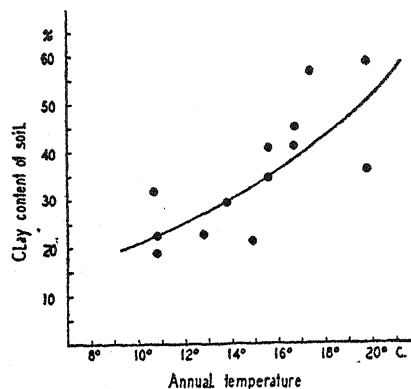


FIG. 5. CLAY-TEMPERATURE FUNCTION FOR THE PARENT MATERIAL GROUP (b) "GNEISSES"

Data adjusted to constant N.S.Q. 400.

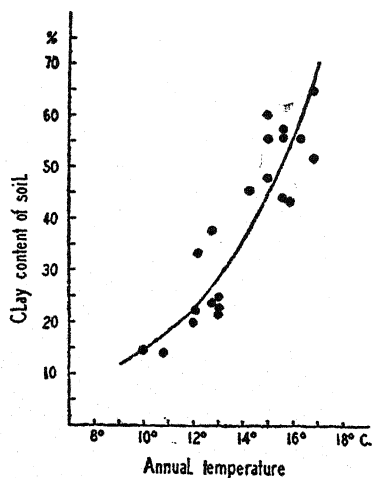


FIG. 6. CLAY-TEMPERATURE FUNCTION FOR THE PARENT MATERIAL GROUP (d) "BASIC ROCKS"

Data adjusted to constant N.S.Q. 400.

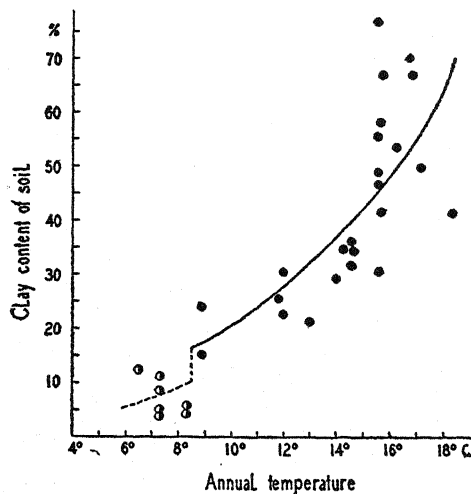


FIG. 7. CLAY-TEMPERATURE FUNCTION FOR THE PARENT MATERIAL GROUP (g) "GRANITES, GNEISSES AND SCHISTS"

Semi-black points refer to soils derived from moraines.

that absurd extrapolations at lower temperatures would result, for instance 0 per cent clay at 8°C. for figure 6. At annual temperatures higher than 20°C.,

equation ( $J$ ) is probably no longer justified because the clay content of a soil can not exceed 100 per cent. Above 20°C. the partial differential coefficient  $\frac{\partial (\text{clay})}{\partial (\text{temp})}$  tends to become zero and some sort of an S-shaped curve is to be expected.

*Relation to Van't Hoff's law*

On thermodynamic grounds, Van't Hoff (8) has suggested that the velocity constant of a chemical reaction depends on temperature probably as follows:

$$\frac{d \ln k}{dT} = \frac{A}{T^2} + B \quad (L)$$

where  $k$  is the velocity constant and  $A$  and  $B$  are functions of temperature. This is Van't Hoff's law, or what he, himself, called "the fundamental equa-

TABLE 10  
Clay-temperature relation for  $N.S.Q. = 400$   
Equation ( $J$ ) (Unglaciated region only)

NUMBER	PARENT MATERIAL	NUMBER OF PROFILES	$a$	$b$	CORRELATION COEFFICIENT $r$
a	Granites	16	0.0961	0.020	+0.737
b	Gneisses	13	0.0388	0.939	+0.760
c	Schists	17	0.0376	1.028	+0.595
d	Basic rocks	21	0.100	0.147	+0.918
e	Granites and gneisses	24	0.0606	0.658	+0.559
f	Gneisses and schists	17	0.0422	0.955	+0.497
g	Granites, gneisses, and schists	24	0.0622	0.686	+0.824

tion." In order to render it suitable for practical purposes it must be integrated, and in this manipulation considerable arbitrariness enters. As a first approach Van't Hoff treats  $A$  and  $B$  as constants and observes experimental agreement by putting either  $A$  or  $B$  equal to zero. In the first case one obtains

$$\frac{d \ln k_1}{dT} = B$$

which gives by integration

$$\ln k_1 = BT \times c$$

or

$$k_1 = c_1 e^{BT} \quad (M)$$

This is known as Berthelot's equation. It indicates that the reaction velocity increases exponentially with rise in temperature. In the second case, by setting  $B = 0$ , one finds

$$\frac{d \ln k_2}{dT} = \frac{A}{T^2}$$

or integrated

$$\ln k_2 = -\frac{A}{T} + c$$

or

$$k_2 = c_2 e^{-\frac{A}{T}} \quad (N)$$

This form also leads to an exponential velocity temperature relation.

It is certain that  $A$ , which includes the heat of reaction, is not a constant, but nearly so for temperatures which are not too far apart, say,  $T_1$  and  $T_2$ . For such a temperature interval Van't Hoff's law takes the form:

$$\ln \frac{k_{T_2}}{k_{T_1}} = A \int_{T_1}^{T_2} \frac{dT}{T^2} = -A \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$$

or

$$k_{T_2} = k_{T_1} e^{A \left( \frac{T_2 - T_1}{T_1 T_2} \right)} \quad (O)$$

This particular equation is known as Arrhenius' temperature law (1). Again the velocity increases exponentially with rising temperature.

Though Van't Hoff's fundamental equation applies only to reactions in which the equilibrium constant ( $k$ ) has a definite meaning, it has been found that many irreversible and living processes exhibit a similar trend between speed of transformation and temperature. In particular it has been observed that in numerous systems a temperature rise of  $10^\circ\text{C}$ . increases the reaction velocity two to three times, a relationship known as Van't Hoff's temperature rule.

It is evident that the clay-temperature curves obtained resemble Van't Hoff's exponential functions. At higher temperatures the clay content of the soil does not increase merely in proportion to temperature, but much more rapidly. As for Van't Hoff's  $10^\circ\text{C}$ . rule, this is obeyed strictly in only three cases (curves b, c, f, table 11) giving quotients 2-3; in two systems (curves e, g) the quotient is about 4, which is not an uncommon value, whereas for the curves (a) and (d) the ratios are very high, namely, 9 and 10.

If the soils south of the glaciated area are considered to be of similar age, the differences in their average clay content will reflect the variations in the velocity of clay accumulation. In accordance with Van't Hoff's law one would

have to conclude that the process of rock decomposition and clay formation is the more rapid the higher the temperature.

A search through the literature reveals that the data presented appear to be the first numerical and statistical proof that the clay content of soils and consequently the profile texture vary with climate, particularly temperature. Many soil scientists have tacitly assumed such a relationship, but several authorities have voiced different opinions. Merrill (7) says, "For many years an impression has prevailed to the effect that rocks decomposed more rapidly in warm and moist than in cold climates . . . such has not yet been proven to actually take place, and indeed many facts tend to prove the impression quite erroneous." Marbut (6) states, "There is no harmonious relationship between soil texture and the environment in which the textures occur. They occur in a wholly hit or miss way in any kind of geographic environment."

Upon a critical survey of the data at hand the author has not been able to

TABLE 11  
*Velocity of clay formation as related to Van't Hoff's temperature rule*  
10°C. interval from 8-18°C.

NUMBER	PARENT MATERIAL	AVERAGE CLAY CONTENT ON THE BASIS OF EQUATION (J)		RATIO CLAY (18°C.) CLAY (8°C.)
		At 8°C.	At 18°C.	
		<i>per cent</i>	<i>per cent</i>	
c	Schists	21.3	50.7	2.4
b	Gneisses	17.7	43.4	2.5
f	Gneisses and schists	19.6	51.9	2.7
e	Granites and gneisses	13.9	56.1	4.0
g	Granites, gneisses, and schists	15.3	63.9	4.2
a	Granites	6.2	56.2	9.1
d	Basic rocks	8.8	88.5	10.0

find a more satisfactory explanation of the clay-latitude correlation than that furnished by the causal rôle of temperature.

#### *The idealized clay-climate surface*

After evaluation of the separate effects of moisture and temperature on clay formation it becomes possible to establish an idealized clay-climate equation which contains both climatic variables and which is of the general form.

$$\Gamma = f(H, T) \quad (P)$$

where  $\Gamma$  represents the average clay content of the soil in per cent,  $H$  the annual moisture value (N.S.Q.), and  $T$  the annual temperature in degrees centigrade. Equation (P) can be written in differential notation as follows:

$$d\Gamma = \left( \frac{\partial \Gamma}{\partial H} \right)_T dH + \left( \frac{\partial \Gamma}{\partial T} \right)_H dT \quad (Q)$$

The partial differential coefficient  $(\partial\Gamma/\partial H)_T$  can be determined with the aid of the clay moisture correlation ( $H$ )

$$\Gamma = mH,$$

or

$$\left(\frac{\partial\Gamma}{\partial H}\right)_T = \frac{\Gamma}{H} \quad (R)$$

The partial differential coefficient  $(\partial\Gamma/\partial T)_H$  follows from equation ( $K$ ) and is

$$\left(\frac{\partial\Gamma}{\partial T}\right)_H = k\Gamma \quad (S)$$

Inserting equations ( $R$ ) and ( $S$ ) into equation ( $Q$ ) one obtains for  $\Gamma$  under the assumption that the constants are independent of climate the following

$$\int \frac{d\Gamma}{\Gamma} = \int \frac{dH}{H} + k \int dT, \quad (T)$$

or

$$\Gamma = cHe^{kT} \quad (U)$$

where  $c$  and  $k$  are constants. On account of the empirical nature of the surface,  $H$  should not be extended over 400, and  $T$  should be restricted to the interval 5–20°C.

In order to arrive at specific values for  $c$  and  $k$  we shall choose the data of the parent material group (e) "granites and gneisses" as given in table 10. The value of  $c$  is found to be 0.014 and that of  $k = 0.140$ , (0.0606 x 2.30). Equation ( $U$ ) becomes

$$\text{Per cent clay} = \Gamma = 0.0114He^{0.140T} \quad (V)$$

and its graph is shown in Figure 8.

The meaning of this clay-climate surface can be stated as follows:

Figure 8 illustrates the relation between clay content of soil and temperature and moisture, in absence of disturbing conditions (absence of glaciation, constancy of other soil forming factors). It applies only to residual soils derived from mixtures of granites and gneisses. In other words, if the entire United States were covered by granites and gneisses the graph would show the variation of the climatic clay content of the soils formed. Naturally the surface is an abstraction and as such not exactly true to nature, but it proves itself of great value in visualizing the distribution of climatic clay and the fluctuations of soil texture under a given set of conditions. In particular, figure 8 yields the following information:



Under conditions of limited moisture the clay content of the soil is very low, regardless of the temperature.

With increasing moisture the clay content increases in proportion to N.S.Q.<sup>3</sup> The rate of increase is greatest in the South and smallest in the North.

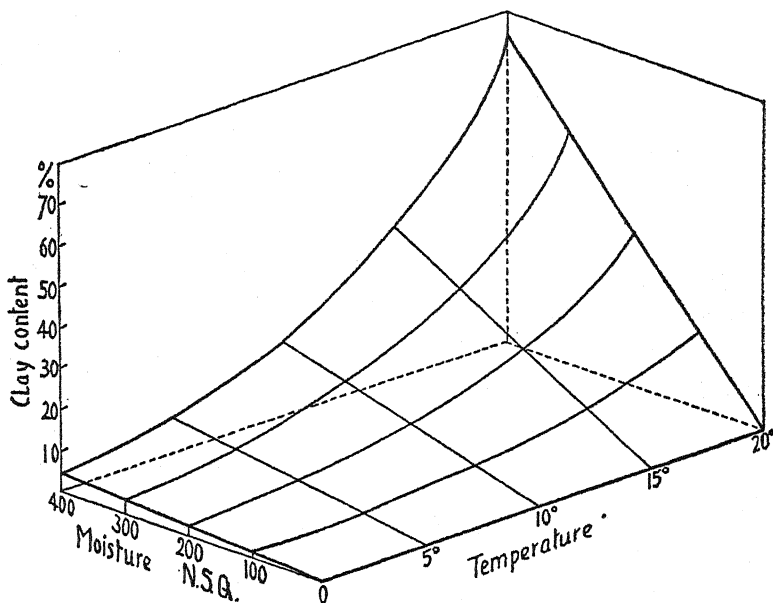


FIG. 8. IDEALIZED CLAY-CLIMATE SURFACE, SHOWING THE VARIATION OF "CLIMATIC CLAY" IN SOILS DERIVED FROM GRANITES AND GNEISSES AS A FUNCTION OF MOISTURE AND TEMPERATURE

TABLE 12

*Clay content (0-40-inch depth) of idealized soils derived from granites and gneisses for selected moisture and temperature values. Constancy of other soil forming factors assumed*

	°C.	INCREASING MOISTURE (N.S.Q.) —————→			
		N.S.Q.			
		100	200	300	400
Increasing temperature ↓	0°	1.1% clay	2.3% clay	3.4% clay	4.6% clay
	5°	2.3% clay	4.6% clay	6.9% clay	9.2% clay
	10°	4.6% clay	9.2% clay	13.9% clay	18.5% clay
	15°	9.3% clay	18.6% clay	27.9% clay	37.2% clay
	20°	18.8% clay	37.5% clay	56.3% clay	(75.0)% clay

With increasing temperature the clay content of the soil increases exponentially. The effect of temperature is most pronounced in the humid region and the least in the arid. Southern soils contain more clay than northern ones (compare table 12).

<sup>3</sup> It is likely that in the subtropics and tropics the function  $\Gamma = f(\text{moisture})$  is not merely a straight line but of logarithmic type [compare reference (5)].

A comparison of the clay-climate surface with the nitrogen-climate function published previously (4) is of interest. In regard to *moisture*, the effect is similar in both instances, namely, an increase in nitrogen and clay with higher N.S.Q. figures. On the other hand, *temperature* has an opposite influence on the two outstanding soil properties. It tends to accumulate clay but lowers the nitrogen and organic matter content. In other words, for the systems under consideration, northern soils are rich in organic matter and poor in clay (climatic), whereas southern soils possess much clay but little organic matter.

#### SUMMARY

The clay contents of 151 soil profiles developed on crystalline rocks in the eastern United States were correlated with climatic factors.

It was observed that within each of seven different groups of parent materials the average clay content of the soil increases from north to south.

Temperature is considered to be the major factor that is responsible for the high clay levels in the South.

For constant moisture values the clay-temperature function is of exponential nature and resembles Van't Hoff's temperature rule.

An idealized clay-climate surface has been constructed which shows the variation of "climatic clay" in soils derived from granites and gneisses as a function of moisture and temperature.

#### REFERENCES

- (1) ARRHENIUS, S. 1889 Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren. *Ztschr. Phys. Chem.* 4: 226-234.
- (2) Bureau of Chemistry and Soils, U. S. Dept. Agr. 1900-1930 Field Operations (Reports and Maps).
- (3) CROWTHER, E. M. 1930 The relationship of climatic and geological factors to the composition of soil clay and the distribution of soil types. *Proc. Roy. Soc. [London] Ser. B.* 107, 30 pp.
- (4) JENNY, H. 1930 A study on the influence of climate upon the nitrogen and organic matter content of the soil. *Missouri Agr. Exp. Sta. Res. Bul.* 152.
- (5) JENNY, H., AND LEONARD, C. D. 1934 Functional relations between soil properties and rainfall. *Soil Sci.* 38: 363-381.
- (6) MARBUT, C. F. 1928 A scheme for soil classification. *Proc. First Internatl. Cong. Soil Sci.* 4: 1-31.
- (7) MERRILL, G. P. 1906 *Rocks, Rock-weathering and Soils.* New York.
- (8) VAN'T HOFF, J. H. 1884 *Etudes de Dynamique Chimique.* Amsterdam.



## SORPTION OF PHOSPHATES BY NON-CALCAREOUS HAWAIIAN SOILS

L. E. DAVIS<sup>1</sup>

*Experiment Station, Hawaiian Sugar Planters' Association*

Received for publication September 18, 1934

An investigation of the chemistry of "phosphate fixation" in Hawaiian sugar cane soils has been pursued primarily with the hope that a contribution to practical agriculture would ensue. In the course of this study sufficient experimental evidence has been obtained to justify the formulation of a tentative theory of this phenomenon.

The pronounced tendency of Hawaiian soils to "fix" applied phosphates was investigated by Crawley (3) as early as 1902, later by McGeorge (10) and more recently by Hance (7) and Ayres (1).

Historical discussions and rather extensive bibliographies have been made available by Weiser (21) and Williams (22). Only such papers as appear immediately pertinent to the discussion will be cited here.

The expression "phosphate fixation," although apparently somewhat crude, is very useful, since no preconception of a mechanism is involved. Since the present study is of a purely chemical nature, it becomes convenient to restrict the expression to measurable chemical relationships. Phosphate fixation is taken to imply the following phenomenon: When a solution of orthophosphates is applied to soil, there is a decrease in the concentration of phosphates in the solution. No considerations of availability of the fixed phosphate to plants are involved in this convention.

*A priori*, four principal ways in which this decrease in concentration might occur are suggested:

I. Cations of soluble salts present in the soil or cations replaced from the soil by those present in the solution form precipitates with the phosphate ions. II. By double decomposition, relatively insoluble soil minerals react to form insoluble phosphates. III. Phosphates are adsorbed at the extensive soil-solution interface. IV. Phosphates are absorbed by the soil minerals to form complex systems in one or more of the solid soil phases.

It is extremely probable that several reactions take place in any soil when phosphates are applied. It is interesting to discover evidence pointing to dominance of one of these types.

In recent years most writers have concluded that phosphate fixation is

<sup>1</sup> The writer wishes to express his appreciation of the advice and criticism of Dr. Francis E. Hance, under whose direction this study was pursued, and of Arthur Ayres and P. L. Gow.

largely due to the formation of insoluble precipitates, rather than to sorption. Following Comber (2) and Fisher (5) the opinion has generally been accepted that Russell and Prescott (18) were in error when they ascribed their results to adsorption. More recently Ford (6), Dean (4), and others have presented evidence which can be interpreted as indicating the formation of complex addition compounds.

#### EXPERIMENTAL STUDIES

Most upland Hawaiian soils are lateritic, with a high content of hydrated iron oxides, a low silica-sesquioxide ratio, a relatively high content of titanium, a moderate supply of magnesium, a low content of calcium, and a moderately acid reaction. Phosphate fixation is very pronounced; in some cases there is little or no crop response to moderate applications of phosphatic fertilizers, but a response to rather large applications.

Results from experiments with two soils of high fixing capacity are discussed in this paper. [Other similar materials have been less extensively studied, particularly by Ayres (1), with consistent results.]

Soil No. 7582—A dark brown surface soil from upper Manoa Valley, on the Island of Oahu.

Soil No. 7512—A yellowish brown subsoil from the northeastern part of the Island of Kauai.

Air-dried, pulverized materials were continuously agitated (usually in an end-over-end tumbler) with solutions of phosphates. Clear filtrates were obtained either by gravity filtration through Whatman No. 12 folded filter paper, by rapid suction through Whatman No. 42 paper, or by filtration under 100 pounds pressure through Chamberland-Pasteur Filter Cylinders No. 7. In the latter case sufficient solution was discarded to allow for the sorption by the cylinder.

In most of the experiments rather high concentrations were employed. The solutions and filtrates were analyzed by the official methods for solutions of fertilizers (A.O.A.C. II). For phosphates the volumetric method was used, for potash the Lindo-Gladding method. pH values were determined either colorimetrically with a LaMotte Roulette Comparator or, when necessary, by a glass electrode. A few exceptions will be noted in the context of each experiment.

The following abbreviations are employed in the tables and figures:

$P_I$  = initial concentration of P in the solution

$P_E$  = concentration of P after agitation of the solution with soil

$\Delta P$  = change in concentration.

Corresponding symbols are used for K and H.

The data are expressed as millimols of solute per liter of solution.

*Rate of fixation*

A 200-gm. portion of air-dried soil No. 7582, passed through a 1-mm. mesh sieve, was agitated with 2 liters of a solution containing 5.0 gm.  $P_2O_5$  as a mixture of  $(NH_4)H_2PO_4$  and  $(NH_4)_2HPO_4$ , 20 gm. of  $NH_4Cl$ , 20 cc. formalin solution, and enough  $NH_4OH$  to bring the pH to 6.8. Small samples of the mixture were removed and rapidly filtered at intervals. The filtrates were then analyzed. The results are presented in table 1. At the end of 16 days the phosphate concentration of the solution had been greatly diminished. Apparently appreciable, but not very large, amounts were still being fixed.

TABLE 1

*Rate of fixation of phosphates*

200 gm. soil no. 7582, 2000 cc. solution, pH = 6.8

TIME	$P_E$	$\Delta P$
Ammonium phosphate and ammonium chloride solutions		
$P_I = 35.20$ millimols per liter		
<i>days</i>		
3	4.08	31.12
7	2.18	33.02
11	1.68	33.52
16	1.34	33.86
After addition of extra phosphate		
$P_I = 29.92$ millimols per liter		
1	24.22	5.70
7	17.60	12.32
14	15.50	14.42
28	11.48	18.44
49	8.94	20.98
85	6.65	23.27

A concentrated solution of ammonium phosphate was then added. After the solution was shaken to effect thorough mixing, a sample was removed and rapidly filtered. The concentration then determined was arbitrarily taken as a new value of  $P_I$ . The mixture was then agitated for 85 days longer with occasional samplings as before. It is evident that at these new concentrations considerably more phosphate was fixed, and that the rate was increased, although it was not nearly so great as the initial rate of the first series. The rate of fixation at any moment is, as one would expect, a function of the concentration in the solution and the amount already fixed by the soil.

A series of separate portions of soil No. 7512 was intermittently agitated with a potassium phosphate solution to which HCl had been added until the

pH was 0.25. The flasks were removed at intervals, the mixtures filtered, and the solutions analyzed. The data are presented in table 2. The pH values are also given. These results will be referred to later in another connection. A continuous agitation of soil No. 7512 (pulverized, and passed through an 80-mesh sieve) with solutions of high and low initial concentrations of phosphate at a pH of 7.0 showed that final equilibrium can be reached in 15 days with continuous mixing.

Although the initial rate of fixation is large, the process does not proceed rapidly to its termination. This condition is quite consistent with the idea that fixation is due to double decomposition or to absorption, but most particularly with the idea that it is due to the latter. It is probably, not necessarily, inconsistent with the hypothesis that fixation is due to precipitation by replaced

TABLE 2

*Rate of fixation of phosphoric acid*

10 gm. soil no. 7512, 100 cc. solution.  $pH_I = 0.25$ .  $P_I = 49.5$  millimols per liter  
Potassium phosphate solutions with added HCl

TIME	$pH_E$	$P_E$	$\Delta P$
1.5 hrs.	0.25	37.5	12.0
3	0.25	36.0	13.5
6	0.25	33.7	15.8
1 day	0.30	30.6	18.9
2	0.50	28.0	21.5
3	0.58	27.2	22.3
4	0.56	26.1	23.4
5	0.58	25.3	24.2
7	0.70	23.9	25.6
9	0.70	22.9	26.6
11	0.70	22.9	26.6
12	0.70	23.2	26.3
14	0.70	22.3	27.2
16	0.70	22.0	27.5
18	0.70	21.7	27.8

bases. A permutite saturated with  $Ca^{++}$  was agitated with potassium phosphate solutions at a pH of 9.6. It had been previously determined that the sodium compound fixed only very small amounts of phosphorus at this pH. In 2 days a state of equilibrium had been attained. This experiment is by no means conclusive since the conditions of exchange in soils may be different from those in the artificial material and an adhering precipitate of calcium phosphate may impede the progress of further exchange in the soil much more than in the permutite.

The very slow attainment of equilibrium in the system implies that other processes than adsorption play a large part in fixation of phosphates, since adsorption equilibria are usually rapidly reached.

*The formal characteristics of equilibria between soil and phosphate solutions*

Portions of finely pulverized soil No. 7512 were continuously agitated with solutions prepared from  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ , and formalin. The period of mixing was 22 days. It is believed, from the results of an experiment described in the foregoing, that a final equilibrium was reached in that time. Four different amounts of soil were used with the same volume of solution. In each of these four series the phosphate concentration was varied. The pH of the solutions was not quite the same in all cases, because of the effect of dilution, but approximated an average of 7.0 for the group. It was impracticable to run the agitations in duplicate, but all analyses were checked by a reexamination of the filtrates at a separate time. The averages of closely agreeing results

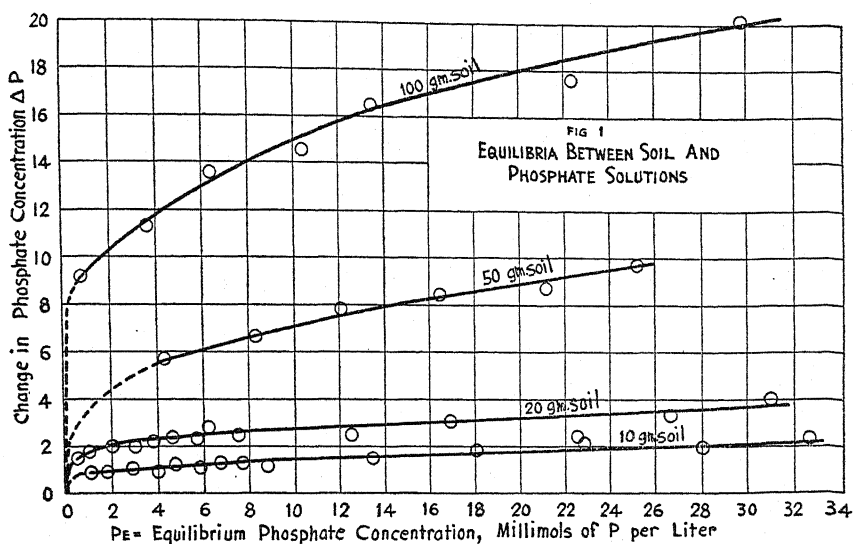


FIG. 1

are presented in table 3 and the function  $\Delta P = F(P_E)$  is plotted in figure 1. The corresponding logarithmic function is plotted in figure 2 for two of the series. The solutions were prepared from a standardized stock solution, and several dilutions were checked by analysis. For this reason the values of  $P_E$  are correctly presented in round numbers. With a fairly high degree of approximation, the curves can be expressed empirically by the function  $\Delta P = kP_E^{1/3}$ , which is Freundlich's adsorption isotherm. On the basis of these curves phosphate fixation could easily be ascribed, as has been done by Russell and Prescott (18), to adsorption by the soil colloids. Fisher (5) has shown that the existence of such curves is not a sufficient criterion and has also stated that chemical precipitations could yield similar curves. Langmuir (8) has shown that adsorptions do not always give a curve of this form. One must certainly agree that since more than one process probably occurs during fixation, too

much stress should not be laid upon the precise form of the curve. Nevertheless, this stricture does not constitute proof that the process is not adsorption; it merely implies the need of corroborative evidence.

Curves of this general form might be expected from theoretical considerations in the case of a number of hypothetical reactions. In all cases the discussion can be simplified by neglecting the increase in concentration which may be due to sorption of pure water.

Let us assume first that calcium present in the base exchange complex precipitates phosphates. Take the simple reaction:

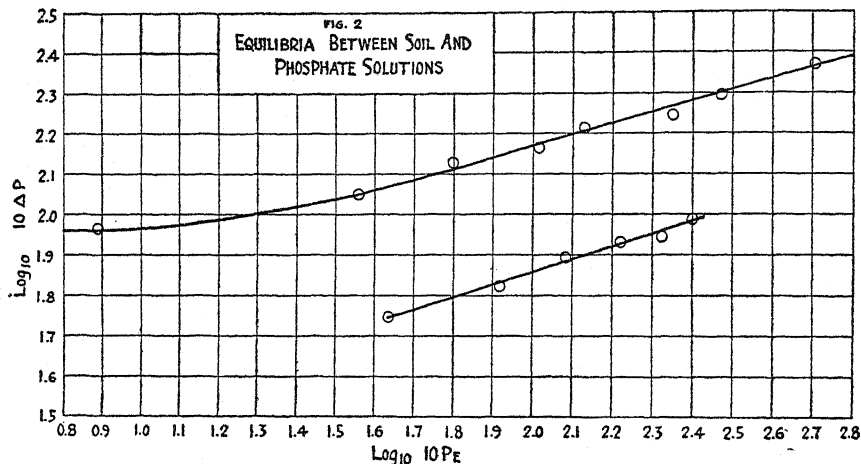
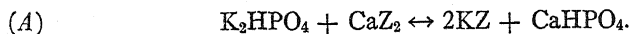


FIG. 2

In the following discussion the theory of Vanselow (20) is accepted. He has presented evidence to show that the various substances present in the base exchange complex (symbolized as  $CaZ_2$ ,  $KZ$ , etc.) probably exist in the complex as mixed crystals and that the activity of each can be considered equal to its mol fraction. If we assume further that the activity of  $K_2HPO_4$  is proportional to its concentration in the solution we can express the equilibrium as follows:

$$(B) \quad k = \frac{\left[ \frac{KZ}{CaZ_2 + KZ} \right]^2}{(K_2HPO_4) \left[ \frac{CaZ_2}{CaZ_2 + KZ} \right]}$$

In any single experiment the initial number of mols of base exchange complex is a constant, i.e.,

$$z = CaZ_2 + \frac{KZ}{2}, \text{ constant.}$$



Also  $P_E = (K_2HPO_4)$ , and the change in concentration,  $\Delta P$ , is equal to the number of mols of  $CaHPO_4$  formed per unit volume of solution, which is again equal to one-half the number of mols of  $KZ$  formed per unit volume of solution, i.e., when  $V$  = volume of the solution;  $\Delta P = \frac{KZ}{2V}$ , and  $CaZ_2 = z - V\Delta P$ , and  $CaZ_2 + KZ = z + V\Delta P$ .

Then

$$(C) \quad k = \frac{4V^2\Delta P^2}{P_E(z - V\Delta P)(z + V\Delta P)}$$

and

$$(D) \quad \Delta P = \frac{z}{V} \sqrt{\frac{kP_E}{4 + kP_E}}$$

If  $kP_E$  is very small compared with 4, the expression assumes very approximately the form  $\Delta P = k' P_E^{1/2}$ .

In any event we can show that the curve should be concave downwards with a steep slope at the origin and a slope approaching zero at the upper limb.

Taking the derivative, we have

$$(E) \quad \frac{d\Delta P}{dP_E} = \frac{2zk^{1/2}}{VP_E^{1/2}(4 + kP_E)^{3/2}},$$

from which

$$(F) \quad \frac{d\Delta P}{dP_E P_E=0} = \infty$$

Also:

$$(G) \quad \frac{d^2\Delta P}{dP_E^2} = -\frac{4zk^{1/2}}{V} \left[ \frac{kP_E + 1}{P_E^{3/2}(4 + kP_E)^{5/2}} \right]$$

Setting the second derivative equal to zero, we get:  $P_E = 1/k$ . The only point of inflection is at a negative value of  $P_E$ ; it therefore has no physical significance. We can see from the negative sign of the second derivative that the curve is concave downward throughout its positive branch.

The preceding discussion was based on the assumption that the activity of  $K_2HPO_4$  is proportional to its concentration, an assumption that will be approximately correct for low concentrations, but not necessarily for high concentrations. Thus it is clear that near the origin the slope will be very great, but it is not certain that we are justified in assuming that the derivation

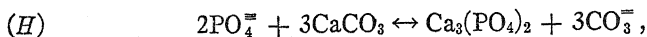
$$\frac{d\Delta P}{dP_E P_E=\infty} = 0, \text{ is physically correct.}$$

However, from general consideration we can derive this result. When  $P_E$  is greatly increased,  $\Delta P$  cannot increase without limit, since its value must

approach as a limit  $z$  or some lesser quantity. Accordingly  $\frac{d\Delta P}{dP_E}$  must approach zero.

From equation (D) we see that for any given value of  $P_E$ , the ordinate on the curve,  $\Delta P$  varies as the ratio  $z/V$ , i.e., as the ratio between the amount of soil and solution. In the curves of figures 1 and 2, this relationship is shown to exist.

If next we consider a possible double decomposition reaction:



then for small concentrations,

$$(I) \quad k = \frac{(\text{CO}_3)^3}{(\text{PO}_4)^2}$$

$$P_E = \text{PO}_4^{=}, \Delta P = \frac{\text{CO}_3^{=}}{3}$$

or

$$(J) \quad \Delta P = \frac{k^{1/3} P_E^{2/3}}{3}$$

and finally

$$(K) \quad \frac{d\Delta P}{dP_E} = \frac{2k^{1/3}}{9P_E^{1/3}},$$

and

$$(L) \quad \frac{d\Delta P}{dP_{E|E=0}} = \infty$$

It cannot be shown quite rigorously that, as  $P_E$  increases greatly, the slope approaches zero, since we do not know how the concentrations vary with the activities. It is exceedingly probable that the curve is concave downward throughout its course, since the second derivative has a negative value:

$$(M) \quad \frac{d^2\Delta P}{dP_E^2} = -\frac{2k^{1/3}}{27P_E^{4/3}},$$

which holds for points close to the origin.

For any given value of  $P_E$ , the ordinate  $\Delta P$  is independent of the mass of the solid reactant (in this case  $\text{CaCO}_3$ ). We should not expect then a series of curves when we vary the ratio of soil to solution, but rather a single curve, the length of which would depend upon the amount of solid present. That is to say, obviously if all the solid is destroyed the curve must terminate.

We find here a very serious objection to the hypothesis that phosphate fixation is largely due to a double decomposition. The situation is by no

means saved by assuming that a number of such reactions occur, since the relative amounts would not be changed by altering the absolute quantities. If at any point one of the solids should be totally consumed, we should get at most a discontinuity in the curve, and not a series of curves.

Finally, let us consider the case of an absorption. It is presumed that a portion of the soil material is of such a character that solutes can penetrate to a slight extent and will be distributed between this material as one phase and the liquid solution as another phase. This hypothesis resembled Vanselow's (20) theory of base exchange. However, in base exchange, from the point of view of the amount of base held by the soil, there is no real significance to the concept of equilibrium between the substrate  $Z^-$ , and the bases (including  $H^+$ ), since in order to have electrical neutrality the substrate must be saturated. The reactions consist not of reactions between substrate and bases but of exchange of bases. The differential equilibria are presumably due to the different activities of the bases and to different degrees of dissociation of the salts formed. In the development of his theory Vanselow has apparently neglected the effect of Donnan equilibria. For the moment a discussion of such effects will be omitted from the following absorption theory.

In the case of phosphate absorption we shall assume, on the contrary, that a reaction occurs between the soil substrate and the phosphate to form new complex compounds. The amounts of these compounds formed will depend upon the activities of the various reactants. It will be convenient to discuss the equilibria due to diffusion of one phosphate ion or compound and reaction with one soil substrate.

If  $P_E$  equals the concentration of a phosphate in the liquid phase, then as long as the activity is proportional to the concentration we can write that the activity is equal to  $iP_E$ . At equilibrium the activities of the phosphate in the two phases must be proportional, according to Henry's law. If  $P_s$  equals the activity of the phosphate in the solid phase, then  $iP_E = sP_s$ , and we can reduce this to  $P_s = hP_E$ .

Let us take the case of a reaction between the phosphate in the solid phase and a component of that phase:



Let  $P_r$  equal the activity of  $PB$ , and  $B_s$  the activity of  $B$ . Then.

$$(O) \quad k = \frac{P_r}{P_s \cdot B_s} = \frac{P_r}{hP_E \cdot B_s}$$

Assume that the activities of all components are equal to their mol fractions in the reactive solid phase. Let  $N$  equal the total number of mols of all substances present, and  $b$  the initial number of mols of  $B$ . Then  $P_r N$ ,  $P_s N$ ,  $B_s N$ , will equal the number of mols of  $PB$ ,  $P$  and  $B$ , respectively, present in the solid phase. Also  $B_s N = b - P_r N$  and,

$$(P) \quad k = \frac{P_r}{hP_E \frac{(b - P_r N)}{N}} = \frac{P_r N}{hP_E (b - P_r N)}.$$

Then

$$(Q) \quad P_r N = \frac{k b h P_E}{1 + k h P_E}$$

Now the total number of mols of the phosphate which have left the solution equals the total number of mols of phosphate which are present in the soil phase at equilibrium. Let  $V$  equal the volume of the solution, which we shall assume has not changed during the reaction. Then

$$(R) \quad V \Delta P = P_s N + P_r N$$

Substituting  $P_s = hP_E$  and (Q), we have

$$(S) \quad \Delta P = \frac{1}{V} \left[ hP_E N + \frac{k b h P_E}{1 + k h P_E} \right]$$

Now  $N$  is a variable. Let  $Q$  be the number of mols of any substances not taking part in the reaction, e.g.,  $H_2O$ , then

$$\begin{aligned} N &= P_s N + B_s N + P_r N + Q \\ N &= P_s N + b - P_r N + P_r N + Q \end{aligned}$$

or

$$(T) \quad N = \frac{b + Q}{1 - P_s} = \frac{b + Q}{1 - hP_E}$$

Then substituting (T) in (S), we have

$$(U) \quad \Delta P = \frac{hP_E}{V} \left[ \frac{b + Q}{1 - hP_E} + \frac{k b}{1 + k h P_E} \right]$$

Now from our knowledge of the very small absorption of chlorides, sulfates, etc. [see Mattson (13)] it is reasonable to suppose that the amount of free phosphate in the solid phases is small also. That is,  $hP_E$  is small compared with unity. The magnitude of  $h$  will depend, of course, upon the unit (mols or millimols, etc.) used for  $P_E$ . For simplicity, let us assume that  $Q$  is small compared with  $b$ . Then we get

$$(V) \quad \Delta P = \frac{hP_E b}{V} \left[ 1 + \frac{k}{1 + k h P_E} \right], \text{ approximately.}$$

Further, if we suppose, in accordance with experimental results, that  $\Delta P$  is of about the magnitude of  $P_E$ , i.e.,  $10^{-1} < \frac{\Delta P}{P_E} < 10$ , we can say that also

$$10^{-1} < \frac{hb}{V} \left[ 1 + \frac{k}{1 + khP_E} \right] < 10.$$

From similar considerations of the amount of soil used per liter of solution we can say that  $b/V$  is of about the magnitude of  $P_E$ . Then  $\frac{hb}{V}$  must, like  $hP_E$ , be very small, and  $\left( 1 + \frac{k}{1 + khP_E} \right)$  must be rather large. Therefore  $\frac{k}{1 + khP_E}$  is large compared with unity, and we can reduce the expression further to:

$$(W) \quad \Delta P = \frac{\frac{k b h P_E}{V}}{1 + k h P_E} = \frac{k_2 P_E}{1 + k_1 P_E}, \text{ approximately.}$$

This expression has the form of Langmuir's adsorption formula (8).

Taking the derivative of (U) we have

$$(X) \quad \frac{d\Delta P}{dP_E} = \frac{h}{V} \left[ \frac{b + Q}{(1 - hP_E)^2} + \frac{kb}{(1 + khP_E)^2} \right].$$

This can also be reduced to the form

$$(Y) \quad \frac{d\Delta P}{dP_E} = \frac{hb}{V} \left[ 1 + \frac{k}{(1 + khP_E)^2} \right]$$

and when  $P_E$  is very small, the slope approaches the value:

$$(Z) \quad \frac{d\Delta P}{dP_{E \rightarrow 0}} = \frac{hb(1 + k)}{V}$$

As  $P_E$  increases in value,  $hP_E$  still being very small as compared with unity, we approach a range where  $khP_E$  becomes large compared with unity and we then have:

$$(AA) \quad \frac{d\Delta P}{dP_E} = \frac{b}{V k h P_E^2}, \text{ approximately.}$$

But since, as we have seen,  $\frac{k}{1 + khP_E}$  is large compared with unity,  $k$  must be large also and as  $P_E$  becomes large the derivative becomes small or

$$(BB) \quad \text{limit } \frac{d\Delta P}{dP_E} = 0.$$

The curve may have a steep slope at the origin, the slope decreasing as the curve is ascended. The logarithmic curve is not linear, as may be shown by taking the logarithm of both sides of (U), giving

$$(CC) \quad \log \Delta P = \log \frac{h}{V} + \log P_E + \log \left[ \frac{b + Q}{1 - hP_E} + \frac{kb}{1 + khP_E} \right]$$

$$(DD) \quad \frac{d \log \Delta P}{d \log P_E} = 1 + hP_E \left[ \frac{\frac{b + Q}{(1 - hP_E)^2} - \frac{k^2b}{(1 + khP_E)^2}}{\frac{b + Q}{1 - hP_E} + \frac{kb}{1 + khP_E}} \right].$$

Again this may be reduced, when  $hP_E$  is small, to the form:

$$(EE) \quad \frac{d \log \Delta P}{d \log P_E} = 1 - \frac{khP_E}{1 + khP_E} = \frac{1}{1 + khP_E}$$

The slope varies between unity and zero, but Langmuir (8) has shown that just this type of curve can be obtained for adsorption of gases. Thus it is quite possible that an adsorption would yield curves similar to those obtained from adsorption.

It will be noted from equation (V) that when  $\Delta P$  is plotted as a function of  $P_E$ , the ordinates will be proportional to  $b/V$ , that is, to the ratio between the amount of soil used and the volume of solution. We have a family of curves with  $b/V$  as a variable parameter.

Since there are possibly present in a natural soil replaceable bases which can precipitate phosphates, as well as more than one absorbent, an interface for adsorption, and more than one phosphate ion,  $H_2PO_4^-$ ,  $HPO_4^{2-}$ , etc., we should in general expect more than one reaction to be possible.

Consider an idealized experiment: A definite amount of a single soil absorbent is treated with a series of solutions of different concentrations, and a curve is drawn. An additional constant amount of soil reactant and sufficient phosphate is now added to each mixture so that the former equilibrium concentration  $P_E$  is reached. The increase in the ordinates will be proportional to the increase in soil reactant, and the resultant curve belongs to the same family as the first curve, with  $b$  as the variable parameter. If now we had added a different soil reactant, the constants  $k$ ,  $h$ , etc. would have become variable also and the resultant curve would generally have had a different analytical form from the original curve. Thus it is possible that the actual experimental curves obtained will not correspond to those characteristic of any single reaction.

To sum up: The form of a single fixation curve experimentally obtained does not certainly imply any particular type of reaction nor necessarily exclude any. The existence of a series of curves for different ratios of soil to solution shows definitely that double decomposition plays a minor part in fixation.

In passing, a few arguments for and against the adsorption hypothesis may

well be discussed. It is known that whereas phosphates are strongly fixed by soils, sulfates and chlorides are not. In soil No. 7582 the sorption of chloride ion was found to follow a very nearly linear function between concentrations of 5 millimols and 5,000 millimols per liter. The percentage sorption was about 3.5, whereas the fixation of phosphates varied from over 80 per cent at  $P_E = 50$  millimols per liter to 99.8 per cent at very small concentrations. This difference is sometimes supposed to be due to the fact that phosphoric acid is tribasic, apparently as the result of a confusion with the well-known fact that the discharging power of ions is a function of their valence. At any rate there is certainly very little trivalent ion present in neutral or acid solutions. Mattson (13) has found that ferrocyanides are not strongly fixed by soil. On the other hand it is objected occasionally that soil colloids are negatively charged and therefore will not adsorb anions. This objection would be pertinent if we considered only electrolytic replacement (polar adsorption). But it is by no means certain that phosphates are not strongly held by non-polar adsorption.

*Reversal of fixation equilibria by dilution of the mixtures*

A pertinent objection to assigning adsorption a dominant rôle in fixation of phosphates is the rather slow rate of such fixation contrasted to the rapid rate of most reactions which are well established as adsorptions. It was observed, however, that mixtures of soil and phosphate solutions became more and more difficult to filter and remained as suspensions longer, as the process of mixing progressed. It was thought possible that, because of progressive dispersion, fresh surface was continuously presented for adsorption.

Alongside the series shown in table 3, in which 50 gm. of soil was agitated with 1 liter of solution, another series was run in which 50 gm. of soil and 500 cc. of solutions, with double the concentration in each case, were shaken for the same time. At the end of this period 500 cc. of water was added to each of the latter series, and the bottles were again shaken for 4 hours. Thus finally the same amount of soil, water, and phosphorous was present in the corresponding members of each series.

The data are presented in table 4 and the results are plotted in figure 3. The columns and curve marked "A" were obtained by interpolation from the curve of the series in which 100 gm. of soil was shaken with 1,000 cc. of solution (see figure 1), since this ratio is equal to that for 50 gm. of soil and 500 cc. of solution. The values of  $P_E/2$  and  $\Delta P/2$  are calculated. This curve then represents the concentrations which should exist immediately upon dilution with 500 cc. of water. The columns and curve "B" represent the data for an agitation of 50 gm. of soil and 1,000 cc. of solution (see figure 1). This is, of course, the ideal for completely reversed equilibria of the series A. The columns and curve "C" represent the actual situation after 4 hours of agitation of the diluted solution.

The equilibria were reversed, but only to a certain extent. Considerations of progressive dispersion do not enter here, and one must suppose that adsorp-

TABLE 3

*Equilibria between soil and phosphate solution*

Soil no. 7512, pH<sub>I</sub> = approximately 7.0. Agitation continuous for 22 days  
Potassium phosphate solutions, 1000 cc.

$P_I$	10 GM. SOIL		20 GM. SOIL		50 GM. SOIL		100 GM. SOIL	
	$P_E$	$\Delta P$	$P_E$	$\Delta P$	$P_E$	$\Delta P$	$P_E$	$\Delta P$
2.00	1.07	0.93	0.54	1.46				
2.75	1.76	0.99	1.01	1.74				
4.00	2.89	1.11	2.00	2.00				
5.00	4.04	0.96	2.96	2.04				
6.00	4.74	1.26	3.78	2.22				
7.00	5.83	1.17	4.61	2.39				
8.00	6.71	1.29	5.67	2.33				
9.00	7.70	1.30	6.17	2.84				
10.00	8.80	1.20	7.46	2.54	4.32	5.68	0.78	9.22
15.00	13.48	1.52	12.48	2.52	8.30	6.70	3.65	11.35
20.00	18.13	1.87	16.87	3.13	12.14	7.86	6.35	13.65
25.00	22.91	2.09	22.56	2.44	16.52	8.48	10.41	14.59
30.00	28.04	1.96	26.65	3.35	21.24	8.76	13.50	16.50
35.00	32.65	2.35	30.96	4.04	25.24	9.76		
40.00							22.37	17.63
50.00							29.77	20.23
75.00							51.52	23.48

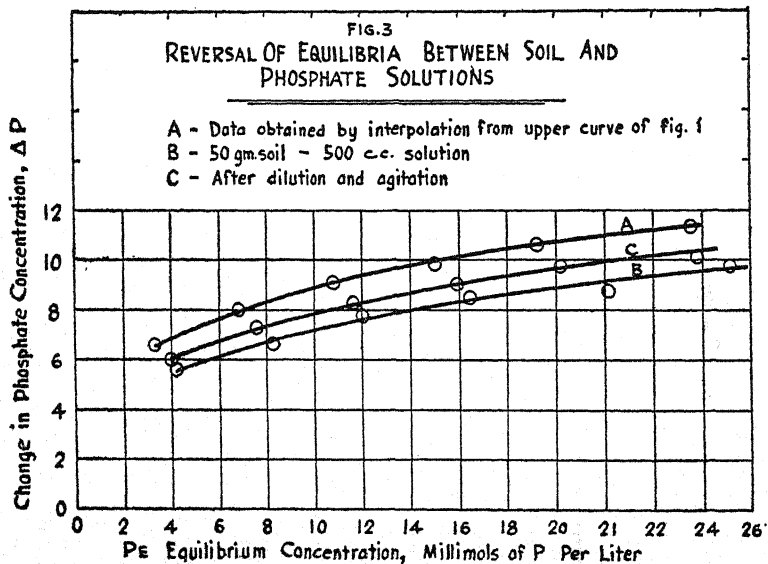


FIG. 3



tion would have been more nearly reversed in 4 hours. It is suggested that we have either reversed an absorption or partially redissolved precipitates formed earlier. Dean (4) has recently shown that phosphorous fixed in soils with a high content of hydrated iron oxides are, like the phosphates of duferinite (a basic ferric phosphate), only rather slowly removed by electrodialysis. One would expect more rapid removal of phosphates if they had been adsorbed.

TABLE 4  
*Reversal of fixation equilibria*  
Soil no. 7512,  $\text{pH}_I = 7.0$

A		B		C	
$P_E/2$	$\Delta P/2$	$P_E$	$\Delta P$	$P_E$	$\Delta P$
3.38	6.62	4.32	5.68	4.04	5.96
6.90	8.10	8.30	6.70	7.65	7.35
10.85	9.15	12.14	7.86	11.69	8.31
15.10	9.90	16.52	8.48	15.96	9.04
19.32	10.63	21.24	8.76	20.24	9.76
23.60	11.40	25.24	9.76	23.87	11.13

A. Results obtained by interpolation from last two columns of table 3—50 gm. soil—500 cc. solution.

B. Results obtained as in table 3 with 50 gm. of soil and 1,000 cc. of solution.

C. Results obtained after dilution of 50 gm. soil and 500 cc. of solution followed by agitation for 4 hours.

*Fixation by soil from which the easily replaced bases have been exchanged for ammonium and potassium ions*

Ammonium ions were substituted for the other bases in the base exchange complex of soil No. 7582 by percolation. Four specimens were prepared as follows:

I. Five liters of  $\text{NH}_4\text{OH}$  solution—1-10—were percolated through 100 gm. of soil. This was followed by a solution containing 10 gm.  $\text{NH}_4\text{Cl}$  per liter, acidified slightly with  $\text{HCl}$ , and later by a solution containing 10 gm.  $\text{NH}_4\text{Cl}$  per liter at a pH of 7.0 until the percolate had a pH of 7.0.

II. Ten liters of 1 per cent  $\text{NH}_4\text{Cl}$  solution at  $\text{pH} = 7.0$  were percolated through 100 gm. of soil until the pH of the percolate was 7.0.

III. A percolation with 5 liters of 0.5  $N$   $\text{HCl}$  was followed by one with a solution of  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$  until the pH of the percolate was 7.0.

IV. One hundred grams of soil was brought to moisture saturation with 1 per cent  $\text{NH}_4\text{Cl}$  solution.

A liter of ammonium phosphate solution at pH 7.0, containing 49.3 millimols of P per liter was added to each of the moist specimens. The mixtures were agitated for 60 hours and were then filtered through filter paper. The results are presented in table 5.

The acid treatment removed considerable amounts of aluminum and iron,

as well as calcium and magnesium; the  $\text{NH}_4\text{OH}$  treatment removed small amounts of aluminum and a great quantity of organic matter.

It appears that the replaceable bases account for only a small fraction, 3.7 per cent, of the phosphate fixed under these conditions.

*Bases present in filtrates after fixation of phosphate*

Four 100-gm. samples of soil No. 7582 were agitated for 24 hours with 1,000 cc. of ammonium phosphate solutions at pH 7.0, containing 10 gm.  $\text{NH}_4\text{Cl}$ . In general this ratio of soil to solution was used in the experiments which are discussed hereinafter. Phosphorus, silica, and certain bases were determined by Paul Chu. The results are presented in table 6.

TABLE 5

*Phosphate fixed by soils treated to exchange  $\text{NH}_4^+$  and  $\text{H}^+$  for other bases*

100 gm. soil 7582, 1000 cc. solutions.  $\text{pH}_I = 7.0$ .  $\text{P}_I = 49.3$  millimols per liter

PREVIOUS TREATMENT	$\text{P}_E$	$\Delta\text{P}$
$\text{NH}_4\text{OH}$ , $\text{NH}_4\text{Cl}$ .....	18.6	30.7
$\text{NH}_4\text{Cl}$ .....	15.4	33.9
$\text{HCl}$ , $\text{NH}_4\text{Cl}$ .....	27.3	22.0
No percolation.....	14.1	35.2

TABLE 6

*Composition of filtrate after agitation of soil and phosphate solutions*

100 gm. soil 7582, 1000 cc. solutions (quantities in millimols per liter)

$\text{P}_I$	$\text{P}_E$	$\Delta\text{P}$	$\text{SiO}_2$	Ca	Mg	Mn	Al	Fe	Ti
0	0	0	0.12	0.94	1.64	0.26	Trace	Trace	None
5.63	0.03	5.60	0.25	0.91	1.60	0.13	Trace	Trace	None
14.10	0.40	13.70	0.45	0.77	1.46	0.07	Trace	Trace	None
70.40	27.10	43.33	1.33	0.05	0.49	0.02	None	Trace	None

We see clearly that precipitates of calcium, magnesium, manganese, and aluminum phosphates have been formed wherever the phosphate concentration was high enough to exceed the solubility products of the various compounds. It is of interest to note that silica is removed by the higher concentrations of phosphates.

*Fixation of basic ions accompanying phosphate ions*

Portions of soil No. 7582 were agitated for 48 hours with solutions of potassium chloride, ammonium chloride, potassium phosphate, and ammonium phosphate. The bases as well as the phosphate were determined and the results are presented in table 7. The last four treatments in the table were agitated for 24 hours instead of 48 hours.

After these results had been obtained all the solutions and filtrates from the final equilibrium experiment obtained with soil No. 7512 (see table 3) were analyzed for potassium. The results are presented in table 8 and plotted in figure 4. It was found that the potash equilibria were reversed like the phosphate equilibria and to about the same extent.

Portions of soil No. 7582 were shaken for 48 hours with a series of ammonium phosphate solutions at pH 6.8 which contained also 10 gm.  $\text{NH}_4\text{Cl}$  per liter. Both P and  $\text{NH}_4^2$  were determined (table 9).

TABLE 7  
Fixation of basic ions  
Soil no. 7582

SALT	pH <sub>I</sub>	P <sub>I</sub>	P <sub>E</sub>	ΔP	K <sub>I</sub> OR (NH <sub>4</sub> ) <sub>I</sub>	K <sub>E</sub> OR (NH <sub>4</sub> ) <sub>E</sub>	ΔK OR ΔNH <sub>4</sub>
KCl.....	6.8				85.1	75.6	9.5
NH <sub>4</sub> Cl.....	6.8				75.3	70.5	4.8
KH <sub>2</sub> PO <sub>4</sub> , K <sub>2</sub> HPO <sub>4</sub> .....	6.8	50.0	16.3	33.7	78.5	32.9	45.6
(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub> , HCl.....	4.0	47.9	12.9	35.0	48.0	21.1	26.9
KH <sub>2</sub> PO <sub>4</sub> , K <sub>2</sub> HPO <sub>4</sub> .....	6.8	52.4	22.0	30.4	78.4	45.1	33.3
KH <sub>2</sub> PO <sub>4</sub> , HCl.....	4.0	52.4	13.4	39.4	78.4	55.7	22.7
(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> .....	6.8	52.6	22.0	30.6	73.5	41.6	31.9
(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub> , HCl.....	4.0	52.6	15.4	37.2	73.5	48.0	25.5

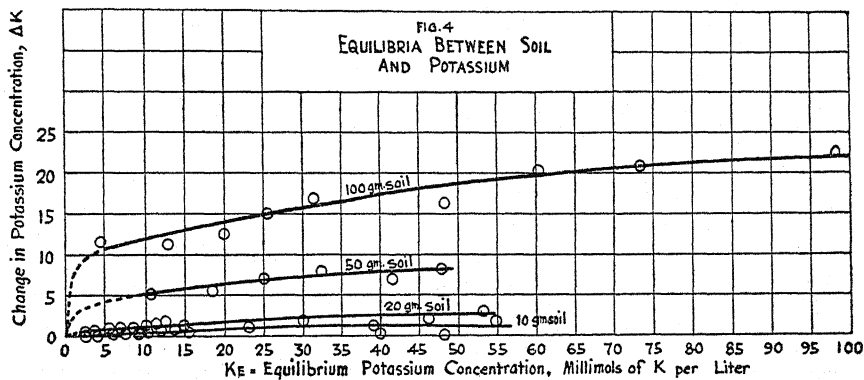


FIG. 4

It is very evident that in the process of fixation of phosphates basic ions are also fixed to a great extent. The amounts of bases (exclusive of H) fixed are roughly proportional to the amounts of phosphate fixed. The relative amounts would depend, of course, upon the amounts of H fixed and would thus vary with the pH of the solutions, as will be shown later. It is significant that where an additional salt was present more of the base was fixed.

<sup>2</sup> The author is indebted to Q. H. Yuen for the determinations of ammonium ion.

The ratio of base to H is greater. The phenomenon is analogous to base exchange.

Soil No. 7582 was treated by percolation in duplicate with the following solutions:

- I. 4 liters 0.001 *N* HCl
- II. 2.5 liters 1.0 KCl
- III. 2.5 liters 1.0 *N* CaCl<sub>2</sub>

TABLE 8

*Equilibria between soil and potassium in potassium phosphate solutions*

Soil no. 7512, pH<sub>I</sub> = approximately 7.0. 1,000 cc. of solutions

10 GM. SOIL			20 GM. SOIL		50 GM. SOIL		100 GM. SOIL	
K <sub>I</sub>	K <sub>E</sub>	ΔK	K <sub>E</sub>	ΔK	K <sub>E</sub>	ΔK	K <sub>E</sub>	ΔK
3.22	2.95	0.27	2.76	0.46				
4.43	4.18	0.25	3.72	0.71				
6.45	5.89	0.56	5.46	0.99				
8.06	7.38	0.68	6.89	1.17				
9.67	8.96	0.71	8.50	1.17				
11.28	10.52	0.76	9.85	1.43				
12.90	12.19	0.71	11.35	1.55				
14.50	13.74	0.76	12.58	1.92				
16.10	15.50	0.60	14.75	1.35	10.75	5.35	4.44	11.66
24.18	22.94	1.24	22.82	1.36	18.50	5.68	12.81	11.37
32.24	30.59	1.65	30.08	2.16	25.00	7.24	19.83	12.41
40.30	39.95	0.35	39.17	1.13	32.40	7.90	25.63	14.94
48.36	48.38	-0.02	46.28	2.08	41.50	6.86	31.36	17.00
56.42	54.75	1.67	53.32	3.10	48.00	8.42		
64.48							48.30	16.18
80.60							60.31	20.29
120.90							98.32	22.58

TABLE 9

*Fixation of bases*

Soil no. 7582, (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, + 1 per cent NH<sub>4</sub>Cl

P <sub>I</sub>	P <sub>E</sub>	ΔP	NH <sub>4</sub> I	NH <sub>4</sub> E	ΔNH <sub>4</sub>
5.63	0.01	5.62	191.2	172.4	18.8
14.08	0.16	13.92	205.6	175.7	29.9
42.24	6.76	35.48	268.0	204.3	63.7
70.40	23.30	47.10	324.7	233.1	91.6

The pH of each solution was adjusted so that in the case of the KCl and CaCl<sub>2</sub> percolations the final portions of the percolate had a pH of 7.0. No calcium was found in the last portions of percolates I and II. The materials were then repeatedly washed with 95 per cent ethyl alcohol until the washings were free from chlorides. A washing with ethyl ether was then followed by

drying with a current of air. The residues were then agitated for 24 hours with potassium phosphate solutions at a pH of 7.0. The results are given in table 10.

These results show conclusively that potassium phosphate is fixed by a sorption process in this soil. In the last case the additional fixation due to the precipitation of calcium phosphate is clearly shown. It is of interest to note that possibly slightly more phosphate was fixed in the soil which had been treated with acid than in that treated with KCl. Also more potash was fixed by the soil treated with HCl than by that treated with  $\text{CaCl}_2$ . It is suggested that the strongly buffered potassium phosphate solution is capable of replacing almost all the  $\text{H}^+$  in the base exchange complex, as well as almost all of the calcium, the latter effect due to removal of  $\text{Ca}^{++}$  to form precipitates. Then if somewhat more phosphate is fixed by an acid soil than by a neutral soil we should expect somewhat more potassium to be fixed also.

TABLE 10

*Fixation of phosphate and potassium by materials in which  $\text{H}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{++}$  had replaced other bases*

Soil no. 7582, experiments in duplicate.  $P_I = 49.06$ .  $K_I = 78.21$

TREATMENT	$P_E$	$\Delta P$	$K_E$	$\Delta K$
HCl.....	29.64	19.42	53.32	24.89
HCl.....	29.99	19.07	53.48	24.73
KCl.....	30.69	18.37	61.46	16.75
KCl.....	30.34	18.72	61.46	16.75
$\text{CaCl}_2$ .....	25.69	23.37	54.55	23.66
$\text{CaCl}_2$ .....	25.98	23.08	54.39	23.82

*Fixation from solutions of different hydrogen-ion concentrations*

A series of potassium phosphate solutions was prepared and adjusted to various pH values by the addition of HCl or KOH, and of KCl, in such a way as to maintain the same concentration of K and P throughout the series.

Both the soils No. 7582 and 7512 were shaken with these solutions for 72 hours. The pH values were determined with a glass electrode. The results are presented in tables 11, 12, and 13. The data in table 13 were obtained at another time, and unfortunately the period of agitation was only 24 hours instead of 72. For this reason the results do not coincide. Also  $\Delta K$  and  $\Delta H$  were not determined. The calculation of  $\Delta H$  from pH values becomes less accurate in this range. The values of  $\Delta H$  are the sums of the changes in H-ion concentration plus the hydrogen absorbed as  $\text{HPO}_4^-$  etc. These quantities have been calculated from the initial and final pH values, and the initial and final concentrations of P by the use of a graph (prepared by P. L. Gow) in which the mol fractions of  $\text{H}_3\text{PO}_4$ , etc., are plotted as functions of the pH.

TABLE 11

*Fixation of phosphate, potassium, and hydrogen from solutions of different pH values*Soil no. 7582,  $P_I = 50.00$  millimols per liter.  $K_I = 96.84$  millimols per liter

$pH_I$	$pH_E$	$P_E$	$\Delta P$	$K_E$	$\Delta K$	$\Delta H$	$\frac{\Delta H + \Delta K}{\Delta P}$
2.03	4.32	6.35	43.65	78.08	18.76	122.4	3.23
3.01	5.45	12.34	37.66	68.87	27.97	84.1	2.97
4.05	5.70	13.65	36.35	66.23	30.61	75.4	2.90
5.02	5.79	13.91	36.09	66.32	30.52	73.0	2.87
6.04	6.87	14.96	35.04	62.37	34.47	70.5	3.00
7.04	7.60	20.26	29.74	59.57	37.27	43.9	2.74
8.03	8.23	23.65	26.35	56.94	39.90	28.1	2.62
9.00	8.50	24.26	25.74	53.73	43.11	25.3	2.67

TABLE 12

*Fixation of phosphate, potassium, and hydrogen from solutions of different pH values*Soil no. 7512,  $P_I = 50.00$  millimols per liter.  $K_I = 96.84$  millimols per liter

$pH_I$	$pH_E$	$P_E$	$\Delta P$	$K_E$	$\Delta K$	$\Delta H$	$\frac{\Delta H + \Delta K}{\Delta P}$
2.03	3.20	18.44	31.56	92.57	4.27	96.3	3.18
3.01	5.45	28.18	21.82	86.39	10.45	64.5	3.44
4.05	5.70	29.39	20.61	84.42	12.42	45.9	2.83
5.02	5.83	29.56	20.44	85.41	11.43	44.0	2.72
6.04	6.75	30.78	19.30	84.83	12.01	47.2	3.08
7.04	7.85	33.39	16.61	82.03	14.81	30.7	2.74
8.03	8.35	35.57	14.43	79.65	17.19	16.1	2.31
9.00	8.90	36.26	13.74	78.58	18.26	13.8	2.34

TABLE 13

*Fixation of phosphates at various low pH values* $P_I = 50.00$  millimols per liter

$pH_I$	SOIL NO. 7582			SOIL NO. 7512		
	$pH_E$	$P_E$	$\Delta P$	$pH_E$	$P_E$	$\Delta P$
3.03	5.45	17.0	33.0	5.28	31.8	18.2
2.72	5.23	15.5	34.5	4.88	31.1	18.9
2.46	4.97	11.1	38.9	4.38	28.9	21.1
2.15	4.59	10.9	39.1	3.45	25.1	24.9
1.95	4.17	8.8	41.2	2.93	22.5	27.5
1.81	3.75	5.6	44.4	2.58	21.3	28.7
1.59	2.83	3.0	47.1	2.20	20.9	29.1
1.41	2.51	4.1	45.9	2.02	22.2	27.8
1.21	2.36	7.7	42.3	1.82	23.5	26.5

The relation between phosphate fixed and the final pH is plotted in figure 5, and the graph is presented as figure 6.

As might be expected on the basis of a sorption theory, the relative amounts

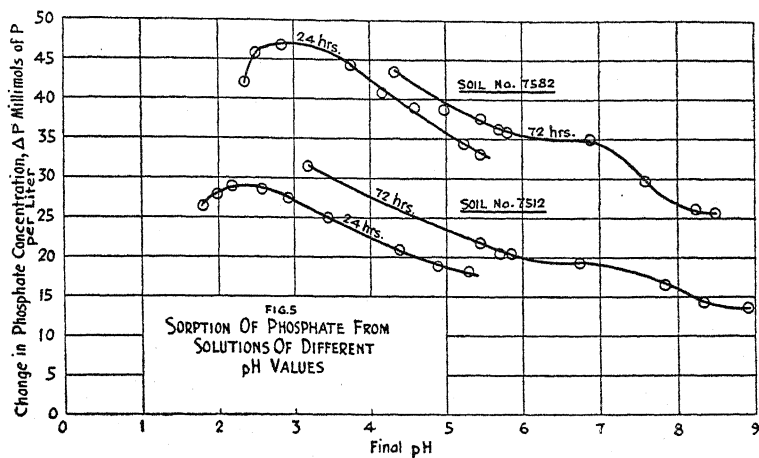


FIG. 5

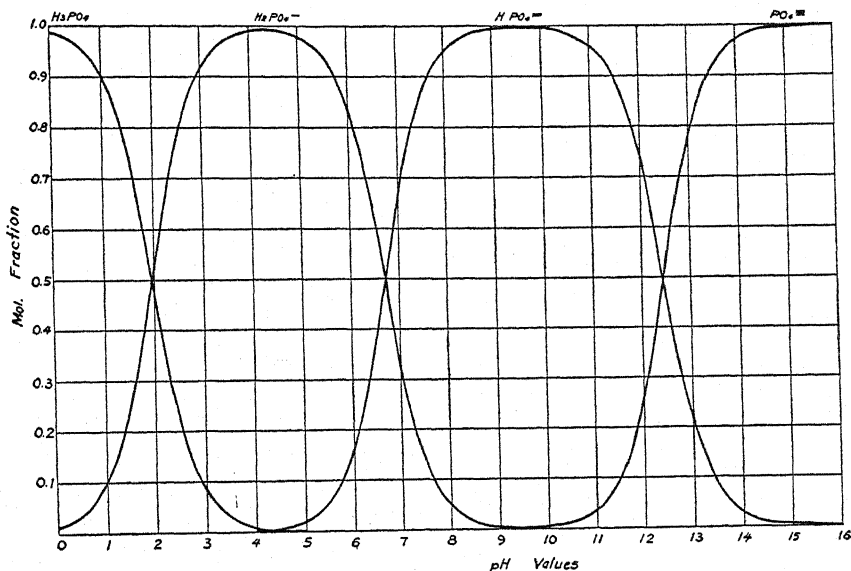
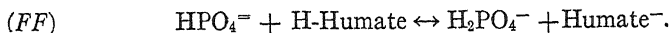


FIG. 6. MOL FRACTIONS OF PHOSPHORIC ACID AND ITS IONS AT VARIOUS pH VALUES

of  $\Delta H$  and  $\Delta K$  vary inversely, and the ratio  $\frac{\Delta H + \Delta K}{\Delta P}$  is approximately equal to 3. The possible accumulation of errors in this ratio (due to analysis and calculation) must be very great. Furthermore, the existence of side reactions

involving exchange of  $H^+$  and  $K^+$  for undetermined cations and those involving the solution of organic matter by the more alkaline solutions would affect this value. In particular, the solution of organic acids would increase the hydrogen present in the solution without altering the concentration of potassium. We can express this process as follows:



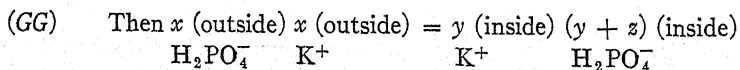
We should then expect that  $\frac{\Delta H + \Delta K}{\Delta P}$  would be decreased in alkaline media, which is seen to be the case in tables 11 and 12.

The amount of phosphate fixed is a function of the hydrogen-ion concentration. This situation would be quite consistent with an adsorption hypothesis, as was shown by Mattson (16), who, however, varied both the pH and the initial phosphate concentrations of his solutions. It is also consistent with an absorption hypothesis, if we assume different absorption constants for each of the series of ions. There is, however, another plausible explanation of this phenomenon.

In the discussion of the absorption hypothesis it was assumed that phosphates would be distributed between the solid and liquid phases in accordance with Henry's Law. This might be approximately true if the new compounds were not ionized. But the theory should be extended for the case where these complexes are ionized. In that case the Donnan equilibria might greatly change the distribution. Furthermore, if the complexes are amphoteric, the distribution would depend upon the pH, according to the principles developed by Mattson (15) in his discussion of the Donnan equilibrium in an amphoteric colloid.

Let us first consider the cases in an acid media, where we should have immobile cations surrounded by mobile anions, in this case  $H_2PO_4^-$  and  $HPO_4^{=}$  and at lower pH values by undissociated  $H_3PO_4$ .

I. Following Mattson (15), let  $z$  be the "concentration" (the concept "concentration," instead of activity or mol fraction is loosely used here, since we are considering only the relative magnitudes of the amounts of  $H_2PO_4^-$ , etc., in the solid and liquid phases, respectively, and are not attempting a quantitative formulation) of  $H_2PO_4^-$  belonging to the immobile cations inside the solid phase, let  $y$  be the concentration of "free"  $H_2PO_4^-$  inside the solid phase, and  $x$  that of the  $H_2PO_4^-$  in the liquid phase. Then  $y$  and  $x$  are the concentrations of the mobile cation,  $K^+$ , inside and outside of the solid phase, respectively. In the concentrated  $KH_2PO_4$  solutions employed in these experiments we may neglect  $H^+$  in comparison with  $K$  for pH values above 3.



and



(HH)

$$x^2 = y(y + z)$$

then

(II)

$$x < y + z$$

or

(JJ)

$$\begin{array}{ccc} \text{H}_2\text{PO}_4^- & < & \text{H}_2\text{PO}_4^- \\ \text{outside} & & \text{inside} \end{array}$$

II. Let  $z$  be the concentration of  $\text{HPO}_4^{=}$  belonging to the immobile cations, let  $y$  and  $x$  be the free  $\text{HPO}_4^{=}$  inside and outside, respectively, then  $2y$  and  $2x$  are the corresponding concentrations of K. Then

(KK)

$$4x^3 = 4y^2(y + z)$$

and

(LL)

$$x < y + z$$

or

(MM)

$$\begin{array}{ccc} \text{HPO}_4^{=} & < & \text{HPO}_4^{=} \\ \text{outside} & & \text{inside.} \end{array}$$

III. Undissociated  $\text{H}_3\text{PO}_4$  will not be affected by the Donnan equilibria. Accordingly, after a certain point, as the pH is lowered and the ratio  $\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$  decreases, we should expect the ratio between phosphate inside and that outside to decrease also.

Let us now consider three cases which might occur in alkaline solutions where we should expect immobile anions.

IV. Let  $z$  equal the concentration of  $\text{K}^+$  belonging to the immobile anions,  $y$  that of  $\text{H}_2\text{PO}_4^-$  (neglecting  $\text{OH}^-$  which will be small where appreciable amounts of  $\text{H}_2\text{PO}_4^-$  are present) inside, and  $x$  that outside  $y$  and  $x$  also represent free K inside and outside. Then

(NN)

$$x^2 = y(y + z)$$

and

(OO)

$$x > y$$

or

(PP)

$$\begin{array}{ccc} \text{H}_2\text{PO}_4^- & > & \text{H}_2\text{PO}_4^- \\ \text{outside} & & \text{inside} \end{array}$$

V. Let  $z$  have the same meaning as in case (IV), let  $y$  and  $x$  refer to  $\text{HPO}_4^{=}$  inside and outside. Then  $2y$  and  $2x$  refer to free  $\text{K}^+$ .

Then

(QQ)

$$4x^3 = y(2y + z)^2$$

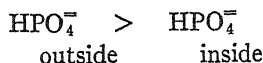
and

(RR)

$$x > y$$

or

(SS)



VI. Considering the case of  $\text{PO}_4^{=}$  ions we have, since  $K = 3y$ , etc.

(TT)

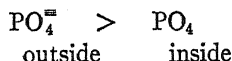
$$27x^4 = y(3y + z)^3$$

(UU)

$$x > y$$

or

(VV)



At very high pH values, the concentrations of  $\text{OH}^-$  will become appreciable; therefore, for a rigorous presentation, they should be included. The expression, however, becomes complicated. The presence of  $\text{OH}^-$  will diminish slightly the tendency for phosphate to be excluded from the solid phase. At the isoelectric point we should expect a simpler distribution corresponding to Henry's Law.

Then considering alone the distribution as we proceed from very low to higher pH values, we should expect first an increase in the phosphate absorbed, then a maximum, then a decrease, and finally a continued decrease at a slower rate. But the amount of phosphate complex and therefore the concentration of  $z$  is a function of  $y$ . Let us assume that we have brought a system of soil and phosphate solution to equilibrium at the isoelectric point. Now, if we acidify the solution we increase the concentration of phosphate ions present in the solid phases, but this also increases the amount of complex formed. Inverse considerations apply to a solution made alkaline. The effects due to the Donnan equilibrium are magnified and we should expect a fairly steep curve with a point of inflection at the isoelectric point, which need not necessarily be the same as the isoelectric point for the soil as a colloidal system.<sup>3</sup>

All these considerations are exhibited in the experimental curves in figure 5. The apparent point of inflection in each curve at  $\text{pH} = 6.5$  approximately may possibly be due to experimental errors. An extended investigation of sorption by a series of soils at different acidities is now under way, and this point, among others, will be then cleared up. The maxima between pH 2 and 4 most probably are augmented by the considerable amount of iron which would go

<sup>3</sup> In the development of this theory the author is indebted to P. L. Gow for his advice and assistance.

into solution and which would precipitate phosphates. For this reason it is questionable to attempt to obtain a final equilibrium in such a range of pH values. The results obtained are to be considered as indicative of what ideally could be expected at final equilibrium if, unfortunately, the acids did not break up the soil material to some extent. Probably it is approximately correct to assume that at any moment during the process of an absorption we have a true equilibrium set up with respect to the depth to which the various ions have penetrated the solid phases, if the reactions are rapid compared to the rate of diffusion.

Midgley (17) has found that  $\text{Na}_2\text{HPO}_4$  is much less readily fixed than  $\text{K}_2\text{HPO}_4$ . If we assume that the more greatly hydrated ions are less firmly held than those less strongly hydrated, that is that the dissociation of a phosphate complex compound follows the lyotropic series for cations, it is possible to explain this phenomenon. In other words the hypothetical sodium phosphate complex is assumed to be more highly dissociated than the corresponding potassium complex. Thus we should expect the Donnan equilibrium effect to be very pronounced. On the other hand, Lohse and Ruhnke (9) found apparently that even  $\text{NaH}_2\text{PO}_4$  was less strongly fixed than  $\text{KH}_2\text{PO}_4$ . However, they were investigating, not equilibria, but the amounts of phosphate extracted by a  $\text{KHSO}_4$  solution in 5 minutes of shaking. The soil treated with  $\text{NaH}_2\text{PO}_4$  was possibly more highly dispersed than that treated with  $\text{KH}_2\text{PO}_4$ . This, taken in conjunction with the fact that the soil was allowed to dry out in contact with the salt solutions instead of being agitated, which would prevent a very deep-seated absorption, would possibly result in a more rapid reversal of the fixation in one case than in another. The author has under way equilibrium experiments in which potassium and sodium phosphates are to be absorbed by sodium and potassium saturated soils under acid and alkaline conditions.

#### *Sorption of phosphates from very acid solutions*

Both of the soils 7582 and 7512 were agitated with very acid phosphate solutions. In an earlier experiment soil No. 7582 was treated with solutions of varying strengths of phosphoric acid for a period of 24 hours. The exact initial and final pH values were not determined. Nevertheless the final pH was probably below 1.0, as judged by the succeeding experiments. The results are presented in table 14.

Samples of both the soils were agitated in a series of flasks with portions of a very acid solution. These flasks were removed from the agitator from time to time. The filtrates were analyzed for phosphates, and the initial and final pH values were determined by the glass electrode. The results for the soil No. 7512 have been presented in table 2.

Of the elements commonly present in soils only one, titanium, could form precipitates in so acid a solution. The solubility of the phosphates of Fe, Al, Ca, and Mg is too great to permit the assumption that they could have been

precipitated, at least with the concentrations of  $\text{H}_3\text{PO}_4$  present. For the sake of completeness this fact was verified by a few simple experiments. A titanium sulfate solution at a pH of 0.45 was added to a phosphate solution at the same pH. Upon shaking, a copious precipitate appeared. It was found that the  $\text{TiO}_2$  content of soil No. 7512 was 9.6 per cent. It therefore seemed possible that the fixation of phosphates in this acid media might be due to precipitation of a titanium phosphate.

However, extraction of this soil with an  $\text{HCl}$  solution maintained at about  $\text{pH} = 0.5$  yielded only a trace of titanium. No precipitate is formed when a

TABLE 14  
*Fixation of Phosphates from solutions at pH values below 1.0*  
Soil no. 7582

$P_I$	$P_E$	$\Delta P$
0	0.74	-0.74
1.41	1.14	+0.27
2.82	1.55	1.27
4.22	2.02	2.20
5.63	2.52	3.11
7.04	3.19	3.85
8.45	3.98	4.47
9.86	4.61	5.25
11.26	5.35	5.91
12.67	6.04	6.63
14.08	6.99	7.09

TABLE 15  
*Fixation of phosphates in very acid solutions in the presence and absence of hydrogen peroxide*  
Soil no. 7512

	$P_I$	$P_E$	$\Delta P$
$\text{H}_2\text{O}_2$ not present.....	239.1	217.4	21.7
$\text{H}_2\text{O}_2$ present.....	242.6	221.3	21.3

titanium solution is added to an acid solution of phosphates containing sufficient hydrogen peroxide. Soil No. 7512 was agitated for 2 hours with two acid phosphate solutions, one of which contained  $\text{H}_2\text{O}_2$ . After filtering, a titanium sulfate solution at pH 0.5 was added to portions of each filtrate. In the one to which no  $\text{H}_2\text{O}_2$  had been added a precipitate was formed. In the other an intense orange-yellow color, but no precipitate, was formed. The phosphate was then determined in appropriate aliquots. The results appear in table 15. The amount fixed is not so great as in other experiments, since the time of mixing was rather short. It seemed desirable not to allow the  $\text{H}_2\text{O}_2$  to be too greatly diminished, as might have occurred over a longer period.

It is quite apparent from these facts that the fixation was not due to the

precipitation of titanium compounds. The remaining possibility is that of a sorption.

#### CONCLUSIONS

Returning to the four hypotheses presented in the introduction, we can eliminate the hypothesis that precipitation by replaced bases plays a dominant rôle in phosphate fixation in these soils because the time for complete equilibria is too great; pronounced fixation takes place in soil freed from replaceable Ca, Mg, etc., and fixation is still very great in very acid solutions in which such phosphates would be soluble. Fixation cannot be largely due to double decompositions because for any given equilibrium phosphate concentration, the amount of phosphate fixed varies very nearly as the ratio of soil to solution; the phosphates are fixed in very acid solutions under such conditions that a double decomposition with calcium, magnesium, manganese, iron, aluminum, or titanium compounds cannot be responsible.

Unless some other possibility remains, we are left with sorption as the only alternative. Between adsorption and absorption, the choice is not so clear. The principal argument against the adsorption hypothesis is the slowness with which equilibrium is attained and reversed. It is possible that a true adsorption may proceed very slowly in some cases, as is true of sorptions by gels, if these are to be considered as adsorptions. In fact, the chief criterion between adsorption and absorption must remain that of the rate of reaction except in two cases: (a) A pronounced sorption occurs in a substrate of very low dispersion and (b) an examination of the material shows that a new mineral substance has been formed. The latter case has appeared in the results of Ford (6), who was able to show by X-ray analysis that in the fixation of phosphates by Goethite and other minerals a new crystal structure had been achieved. It is not clear that Ford considered his results to be due to absorption. It would seem very probable that they were due to absorption; almost certainly they were not due to adsorption. This method is probably not practicable with complex materials like soils. Nevertheless, the analogy is not at all unreasonable; it would seem very unlikely that if phosphates are absorbed more or less by hydrated minerals of known composition they would not likewise be absorbed by similar hydrated minerals of the soil.

As far as the mechanism of sorption goes, it is possible that there is little or no true distinction between adsorption and absorption of phosphates by minerals. It is very probable that we have to reckon here with attractive forces more akin to those studied in inorganic chemistry than with those present in the case of the adsorption of gases by charcoal (with the exception of the sorption of oxygen). It is believed that this conclusion is in accord with the views of Mattson (12, p. 396, and elsewhere). The author feels that a careful reading of the profound series of papers by Mattson upon the part of those who still ascribe anion fixation almost exclusively to precipitation will cause doubts of that hypothesis to arise. It must, however, be remarked that

very probably in many soils, notably the alkali soils studied by McGeorge and Breazeale (11) and others, precipitation by interaction with alkaline earth carbonates and by replaced bases is of outstanding importance.\*

The chief distinction between the two types of sorption lies in the deep seated character of absorption. A study of the effect of increased dispersion upon equilibrium with phosphate solutions might enable one to decide whether there is a diffusion into the solid phase. At present, the author feels that all the evidence supports the hypothesis of an absorption, with, of course, some adsorption.

Very tentatively the following picture is suggested to explain phosphate fixation in soils freed from exchangeable Ca, Mg, etc.:

Phosphates penetrate the liquid-solid phase interface and form new compounds with the hydrated minerals, similar to those suggested by Mattson (14, p. 471) or possibly Werner coördination compounds. These compounds have activities which are a function of their mol fractions, and exist in equilibrium with the hydrated minerals and the phosphate compounds. This suggestion seems superior to the idea of a whole series of individual compounds of varying phosphate content. These compounds can be considered as salts and potentially ionized; the anion is of low mobility; the cations, K,  $\text{NH}_4$ , etc., are interchangeable. Thus we produce an increased base exchange complex. In addition, cations and anions are distributed between the liquid and solid phases in accordance with Donnans' theory. In accordance with this, we should expect the amount of phosphate fixed to be dependent upon the pH of the solution.

Reaction conditions are similar at the interface. Two cases may occur: (a) hydroxyl groups oriented outward in a negative surface are replaced by phosphate ions with an increase in negative potential, (b) metal ions oriented outward react with phosphate ions so that the latter are oriented outward, thus reversing the potential in the rarer cases when positive colloids are present in the soil (as in acid solutions) or in any event overcoming the mutual flocculation formerly caused by the excess of negative colloids and thus increasing the dispersion.

The exact nature of the compounds formed remains a mystery. Except for illustrative purposes there is little to be gained by the pursuit of the facile art of writing imaginary formulas. The mystery is, however, no greater than that surrounding the specific nature of the interfacial systems studied in colloidal chemistry.

#### SUMMARY

An intensive study was made of phosphate fixation in two typical upland Hawaiian soils.

Equilibrium between phosphate solutions and soils was attained only after many weeks.

Final equilibrium curves were obtained with one of the materials.

It was shown that the characteristic "adsorption" curves obtained are ambiguous; they might imply any type of reaction.

For any given equilibrium concentration of phosphates, the amounts fixed are proportional to the ratio of soil to solution employed in the experiments. This is held to be a decisive objection to the possibility that the process is due to double decomposition.

Fixation is reversed very slowly. The slow rate of both the direct and indirect processes casts a doubt upon the ascription of the phenomenon to adsorption.

Pronounced fixation occurs in soil from which the replaceable bases have been exchanged for alkali metal ions.

Cations are absorbed along with the phosphate. At various pH values a ratio of 3 equivalents of cations to 1 mol of phosphorus holds approximately.

The degree of fixation is a function of the hydrogen-ion concentration of the solution.

Fixation occurs to a large extent in solutions maintained at a pH of 0.70 to as low as 0.25.

It is tentatively concluded that phosphate fixation in soils artificially depleted of replaceable bases which can precipitate phosphate is due to absorption of the phosphate by the soil minerals and the formation of equilibrium complexes. In many soils not so depleted this process nevertheless predominates.

A theoretical basis for the fact that the amount of phosphate fixed is dependent upon the pH of the solution is developed in accordance with the Donnan equilibria.

#### REFERENCES

- (1) AYRES, A. 1934 Phosphate fixation in Hawaiian soils: II. *Hawaii. Planters' Rec.* 38: 131-145.
- (2) COMBER, N. M. 1925 The rôle of the electronegative ions in the reactions between soils and electrolytes. *Trans. Faraday Soc.* 20: 1-6.
- (3) CRAWLEY, J. T. 1902 Fixation of phosphoric acid in soil. *Jour. Amer. Chem. Soc.* 24: 1114-1119.
- (4) DEAN, L. A. 1934 Electrodialysis as a means of studying the nature of soil phosphates. *Soil Sci.* 37: 253-266.
- (5) FISHER, E. A. 1922 The phenomena of absorption in soils: A critical discussion of the hypotheses put forward. *Trans. Faraday Soc.* 17: 305-316.
- (6) FORD, M. C. 1933 The nature of phosphate fixation in soils. *Jour. Amer. Soc. Agron.* 25: 134-144.
- (7) HANCE, F. E. 1933 Phosphate fixation in Hawaiian soils. *Hawaii. Planters' Rec.* 37: 182-196.
- (8) LANGMUIR, IRVING 1918 The adsorption of gases on plane surfaces of glass, mica, and platinum. *Jour. Amer. Chem. Soc.* 40: 1361-1403.
- (9) LOHSE, H. W., AND RUHNKE, G. N. 1933 Studies on readily soluble phosphate in soils: III. The effect of phosphate treatment. *Soil Sci.* 36: 303-316.
- (10) MCGEORGE, W. T. 1922 Phosphate in Hawaiian soils. The combinations and their availability. *Hawaii. Planters' Rec.* 26: 11-27.

- (11) McGEORGE, W. T., AND BREAZEALE, J. F. 1932 Studies on iron, aluminum and organic phosphates and phosphate fixation in calcareous soils. *Ariz. Agr. Exp. Sta. Tech. Bul.* 40.
- (12) MATTSON, SANTE 1929 The laws of soil colloidal behavior: II. Cataphoresis, flocculation and dispersion. *Soil Sci.* 28: 373-409.
- (13) MATTSON, SANTE 1929 The laws of soil colloidal behavior: I. *Soil Sci.* 28: 179-220.
- (14) MATTSON, SANTE 1930 The laws of soil colloidal behavior: III. Isoelectric precipitates. *Soil Sci.* 30: 459-495.
- (15) MATTSON, SANTE 1931 The laws of soil colloidal behavior: V. Ion adsorption and Exchange. *Soil Sci.* 31: 311-331.
- (16) MATTSON, SANTE 1931 The laws of soil colloidal behavior: VI. Amphoteric behavior. *Soil Sci.* 31: 343-365.
- (17) MIDGLEY, R. R. 1931 The movement and fixation of phosphates in relation to permanent pasture fertilization. *Jour. Amer. Soc. Agron.* 23: 788-799.
- (18) RUSSELL, E. J., AND PRESCOTT, J. A. 1916 The reaction between dilute acids and phosphorus compounds of the soil. *Jour. Agr. Sci.* 8: 65-110.
- (19) TEAKLE, L. J. H. 1928 Phosphate in the soil solution as affected by reaction and cation concentrations. *Soil Sci.* 25: 143-162.
- (20) VANSELOW, A. P. 1932 Equilibria of the base exchange reactions of bentonites, permutes, soil colloids and zeolites. *Soil Sci.* 33: 95-113.
- (21) WEISER, V. L. 1933 Fixation and penetration of phosphates in Vermont soils. *Vt. Agr. Exp. Sta. Bul.* 356.
- (22) WILLIAMS, C. O. 1929 The fixation of phosphates in soils. *Union So. Africa Dept. Agr., Div. Chem., Ser.* 100: 426-438.



# A NEW METHOD OF ESTIMATING EXCHANGEABLE BASES IN SOILS

AMAR NATH PURI

*Irrigation Research Institute, Lahore (India)*

Received for publication August 20, 1934

The importance of exchangeable bases in soils needs no emphasis. It is well known that a large amount of food material in soils for the use of plants resides in the exchange complex and some of the most fertile soils are those rich in exchangeable bases. A knowledge of the nature and amount of exchangeable bases is of prime importance in all studies of the relation between soil conditions and plant growth.

Analytical methods for the estimation of exchangeable bases are tedious and time-consuming. Besides, their accuracy is doubtful in the case of saline, alkali, and calcareous soils. The principle of almost all these methods is the same, i.e., the replacement of exchangeable ions in the soil by a single ion through prolonged leaching with its neutral salt. NaCl, KCl, BaCl<sub>2</sub>, NH<sub>4</sub>Cl, and ammonium acetate in water or alcoholic solution have been suggested by different workers for this purpose. Of these, ammonium acetate is perhaps the most favored because of the ease with which it can be removed from the leachate prior to the estimation of the various bases. Some of the errors involved in these estimations in the case of calcareous and alkali soils are avoided by the use of alcoholic solutions, or by estimating Ca in a second liter of the leachate with the neutral salt and allowing for the soluble CaCO<sub>3</sub>. All these precautions, however, make the estimations more cumbersome and are adopted with reluctance when a large number of estimations have to be completed in a comparatively short time.

The writer has recently advocated the use of Ba(OH)<sub>2</sub><sup>1</sup> or ammonium carbonate<sup>2</sup> for the estimation of exchangeable Na and K in soils. Further work in this direction has shown that in ammonium carbonate we have an extremely useful reagent for the estimation of all the exchangeable ions commonly met with in soils. Its use makes these estimations not only simpler but free from objections that can be raised against other methods. It can be used with success for practically all types of soils.

In order to explain the working of the ammonium carbonate method it is nec-

<sup>1</sup> Puri, A. N. 1933 A new method for estimating replaceable Na and K in soils. *Soil Sci.* 26: 355.

<sup>2</sup> Puri, A. N. Estimation of replaceable Na and K, exchange capacity, and degree of alkalization in alkali soils by ammonium carbonate extraction. To be published in *Soil Sci.*

essary to offer some preliminary remarks on its action on a soil containing all the four exchangeable bases, i.e., K, Na, Mg, Ca. Ammonium carbonate solution replaces from the soil all these bases, which appear as carbonates. However, on account of the limited solubility of  $\text{CaCO}_3$  in ammonium carbonate solution only K, Na, and Mg carbonates come in solution and appear in the filtrate. If the filtrate is evaporated to dryness all the ammonium carbonate disappears, leaving behind a residue of K, Na and Mg carbonate with a small amount of  $\text{CaCO}_3$ . Sodium and potassium carbonates can be easily separated from magnesium carbonate, because the first two are soluble in 50 per cent alcohol, the last is not. Since the remaining  $\text{MgCO}_3$  is mixed with some  $\text{CaCO}_3$ , advantage is taken of the limited solubility of the latter in ammonium carbonate solution, in which  $\text{MgCO}_3$  is fairly soluble, to separate the two by extracting with  $N (\text{NH}_4)_2\text{CO}_3$ .

It is to be remembered that ordinary ammonium carbonate contains some ammonium carbamate which can result in the formation of soluble Ca carbamate. All solutions of this reagent, therefore, must be heated to  $60^\circ\text{C}$ .

TABLE 1  
*Amounts of Mg added to, and recovered from, soil by ammonium carbonate*

Mg ADDED	Mg RECOVERED
m.e.*	m.e.*
5	7.4
10	11.9
15	15.6
20	18.9

\* Per 100 gm. soil.

before use. Once the solution has been heated to that temperature carbonate does not go back to carbamate on cooling.

The correctness of the foregoing statements in the case of Na and K replacement by ammonium carbonate has been established elsewhere.<sup>2</sup> In the case of Mg it was proved by working with soils which were made unsaturated and to which known amounts of Mg were then introduced in the replaceable form and determined by the ammonium carbonate method. The following example will make the point clear. A black cotton soil of high base-exchange capacity and containing 54 per cent clay was rendered unsaturated by exhaustive treatment with 0.05  $N$  HCl followed by leaching with water and drying. To 10-gm. portions of this soil in water suspension increasing amounts of  $\text{MgCO}_3$  were added, and the suspension was boiled for 2 hours. It was then leached with 500 cc. 0.5  $N$   $(\text{NH}_4)_2\text{CO}_3$  solution, and Mg was determined as described under "Detailed description of the method."

Table 1 shows the amount of Mg added and recovered by the ammonium carbonate method. Since solid  $\text{MgCO}_3$  was weighed and added to the soil there is likelihood of some error being introduced on that account; the two

sets of results, therefore, may be taken as fairly close. In another soil to which 10.5 m.e. of Mg per 100 gm. of soil was added, the amount recovered was 10.4 m.e. and 9.6 m.e. in duplicate. This soil contained 7 m.e. of Na and K and 25 m.e. of Ca per 100 gm.

#### DETAILED DESCRIPTION OF THE AMMONIUM CARBONATE METHOD

The proposed method is slightly varied according as the soil contains or does not contain  $\text{CaCO}_3$ .

##### *For soils free from $\text{CaCO}_3$*

Portions of soil weighing 10–20 gm. are leached with 500 cc. of 0.5  $N$   $(\text{NH}_4)_2\text{CO}_3$  in 100-cc. lots. The leachate is evaporated to dryness on a sand bath or in an air oven. The residue is taken up with 50 per cent alcohol and filtered. The filtrate with washings is evaporated to dryness, and the residue, after being dissolved in standard acid and brought to the boiling point, is titrated with standard alkali, brom thymol blue being used as indicator. This titration value gives the amount of exchangeable Na and K. If K is required separately, it can be determined in the liquid after titration by any of the standard methods for the estimation of K.

The residue on the filter paper, after the alcoholic extraction, is leached with  $N$   $(\text{NH}_4)_2\text{CO}_3$  warmed above  $60^\circ\text{C}$ . The filtrate is evaporated to dryness and titrated with standard alkali after the addition of an excess of standard acid and heating to the boiling point. This titration value gives exchangeable Mg. The residue on the filter paper is dissolved in a little semi-normal acetic acid and mixed with the acid leachate for Ca. This acid leachate, which is obtained by leaching the soil after the ammonium carbonate treatment with 500 cc. of semi-normal acetic acid in 100-cc. lots, contains all the exchangeable Ca, which, in turn, is determined by the usual permanganate method. Alternately a separate 10–20 gm. of the soil may be taken and exchangeable Ca determined by leaching with  $N$   $\text{NH}_4\text{Cl}$  or semi-normal acetic acid.

It might be pointed out that the problem of estimating exchangeable Ca in soils free from  $\text{CaCO}_3$  has never presented any serious difficulty, and almost any method could be used with equal success. It is for soils containing  $\text{CaCO}_3$  that special precautions have to be adopted to allow for the solubility effects.

##### *For soils containing $\text{CaCO}_3$*

In this method Ca cannot be determined directly in soils containing  $\text{CaCO}_3$ . The indirect determination is not only simpler but more reliable because of its freedom from solubility effects. The soil on the filter paper, after ammonium carbonate treatment for the estimation of exchangeable Na, K, and Mg, is leached with 500 cc. of 0.2  $N$   $\text{KCl}$  in 100-cc. lots. The filtrate is discarded. The soil is again leached with 500 cc. of semi-normal ammonium carbonate in 100-cc. lots. The filtrate is evaporated to dryness and taken up with freshly boiled hot distilled water and filtered. The residue on the filter paper

is washed with hot water. If on the addition of water to ammonium carbonate residue, the solution is dark colored some  $\text{BaSO}_4$  pro-Röntgen is added to it before filtering.<sup>3</sup> The filtrate with washings is titrated residually with

TABLE 2

*Replaceable bases in calcareous soils as determined by the ammonium carbonate method with a comparison of exchangeable Ca as determined by the KCl method*

SOIL NUMBER	LOCALITY	pH VALUE	REPLACEABLE BASES (( $\text{NH}_4$ ) <sub>2</sub> CO <sub>3</sub> METHOD)			REPLACEABLE Ca (KCl METHOD)
			Na and K	Mg	Ca	
			m.e.*	m.e.*	m.e.*	m.e.*
1	Pusa (Bihar)	8.41	0.15	0.15	3.95	5.10
2	Akola (Bombay)	8.21	2.20	3.95	52.35	49.90
4	Punjab	8.55	0.50	0.85	7.05	6.25
5	Punjab	8.77	0.80	0.70	6.10	6.00
7	Punjab	9.58	6.35	0.55	1.40	0
8	Madras	8.41	0.80	0.70	16.90	16.70
10	Madras	8.71	2.35	0.59	19.16	19.25
11	Madras	8.77	0.85	1.20	21.45	22.25
13	Nagpur C.P.	8.53	1.30	0.85	53.80	49.20
16	Lyalpur (Pb.)	8.74	0.50	0.20	4.10	3.50
17	Kalyanpur (U.P.)	8.20	0.20	0.20	7.80	7.65
19	Burma	8.40	1.40	5.25	19.50	16.80
21	Burma	8.25	0.50	0.65	10.45	8.80
24	Meerut (U.P.)	8.59	0.60	0.50	6.35	4.40

\* Per 100 gm. soil.

TABLE 3

*Exchangeable Mg in  $\text{MgSO}_4$ -treated fields after 3 years compared with control plots*

MgSO <sub>4</sub> -TREATED FIELDS—NUMBER	EXCHANGEABLE MG, M.E. PER 100 GM. SOIL
225	1.00
207	1.00
217	1.30
219	1.30
CONTROL PLOTS—NUMBER	
221	0.65
222	0.65
227	0.75
211	0.80

standard alkali after excess of standard acid has been added. The titration value thus obtained is equivalent to the total exchangeable bases in the soil, and, if we subtract from it the value for exchangeable Na, K, and Mg already

<sup>3</sup> Very dark colored residues should be ignited before being taken up with water.

obtained, we get the equivalent of exchangeable Ca. Alternately for the total exchangeable bases a separate 10–20 gm. of soil may be taken and immediately leached with 500 cc. semi-normal KCl in 100-cc. lots followed by leaching with semi-normal ammonium carbonate.

If a soil contains  $\text{CaSO}_4$  but no  $\text{Na}_2\text{SO}_4$ , then before ammonium carbonate leaching some  $\text{Ba}(\text{OH})_2$  should be added; this converts all the  $\text{CaSO}_4$  into insoluble  $\text{BaSO}_4$  and  $\text{Ca}(\text{OH})_2$ . When ammonium carbonate is added, the latter, as well as excess of  $\text{Ba}(\text{OH})_2$  is converted into carbonates and thus rendered harmless. If, however, the soil contains both  $\text{CaSO}_4$  and  $\text{Na}_2\text{SO}_4$  then the latter must be removed by leaching with water before ammonium carbonate treatment.  $\text{Na}_2\text{SO}_4$  alone has no effect and need not be removed from a soil before estimating exchangeable bases by this method.

In order to see how far this indirect method for Ca agrees with any of the other standard methods, exchangeable Ca was determined in a number of soils and compared with the value for Ca obtained by semi-normal KCl leaching. The leachate was collected in two 500-cc. lots, and Ca in the second leachate was subtracted from the first to allow for the solubility effect. The results of this comparison are recorded in table 2. Considering that the KCl method is admittedly subject to errors due to solubility effects, the agreement is fairly close, and as the whole estimation is reduced to simple titrations the method should commend itself to soil workers for routine analyses in connection with survey work.

As an example of the practical application of the method may be mentioned the results of estimations of replaceable Mg from experimental fields to which  $\text{MgSO}_4$  was applied 3 years ago. Table 3 shows that Mg-treated fields still contain a slightly larger amount of exchangeable Mg than do the control plots.

#### SUMMARY

Ammonium carbonate is shown to be a very useful reagent for estimating exchangeable bases in soils.

By the method outlined in the paper the determination of exchangeable bases is reduced to simple titrations, thus making possible such estimations with the minimum of equipment and skill.

The method is especially suitable for the study of saline, alkali, and calcareous soils, which have always presented peculiar difficulties in such estimations.



# A COMPARISON BETWEEN THE SUCTION METHOD AND THE CENTRIFUGE METHOD FOR DETERMINING THE MOISTURE EQUIVALENT OF SOILS<sup>1</sup>

GEORGE JOHN BOUYOUCOS

*Michigan Agricultural Experiment Station*

Received for publication September 17, 1934

In a former communication (2) the suction method was suggested as a simple, rapid, and convenient method for determining the comparative moisture holding power, or moisture equivalent, of soils. The principle of the method consisted of using the suction force of water from a faucet to pull the water from the soil instead of the centrifugal force developed in a centrifuge. Because the method is so simple, convenient, easily available, and inexpensive, it has created considerable interest, and the question has been raised: How do the results of this suction method compare with those of the standard moisture equivalent method as developed by Briggs and McLane (3) wherein the saturated soil is centrifuged at a speed to produce a force 1,000 times gravity?

It is the object of this paper to present the suction method as finally developed upon further investigation, and to compare the results it yields with those obtained by the centrifuge method of Briggs and McLane.<sup>2</sup>

## DESCRIPTION OF METHOD

The original suction method has undergone considerable improvement in details of technique. The final procedure adopted consists of filling a small Büchner funnel, 5 cm. in diameter and 2½ cm. in depth, with air-dry soil that has been passed through a 2-mm. sieve. Care is taken to compact the soil by tapping gently the lower end of the funnel against the table. The filled funnel is placed in a beaker into which water is poured until it almost reaches the level of the soil. After the soil has soaked for about 24 hours, the funnel is placed on a suction flask (plate 1), which is then connected either to the filter pump or to the vacuum pump, and suctioned for 15 minutes after all the free or excess water at the top of the soil has disappeared. The funnel is then removed from the suction flask, the soil scraped into a weighed receptacle, and its moisture content determined in the usual standard way. During suction,

<sup>1</sup> Journal Article 187 N.S., Michigan Agricultural Experiment Station.

<sup>2</sup> In the comparison of the two methods the writer is indebted to Dr. H. E. Middleton of the U. S. Bureau of Chemistry and Soils, and to Dr. Joseph Oskamp of Cornell University, who kindly ran the moisture equivalent of several soils selected for comparison.

the soil is covered with a tumbler containing a moist cloth to prevent evaporation from the soil.

The percolation of the water under suction is very rapid at first in nearly all the soils, but after 5 minutes it becomes very slow, and at the end of 10 minutes only a drop falls about every 2 to 4 minutes.

In the centrifuge method, approximately a 30-gm. sample is used in the case of all mineral soils, regardless of texture. In the suction method, the attempt was made to maintain the same depth of wet soil and not the same weight of dry soil. When the same weight of dry soil is used, the depth of the soil column will vary considerably, as a result of the different degrees of swelling of the various soils upon taking up water. The same depth of soil column was maintained in the suction method by leveling off the soil even with the top of the funnel after the soil was suctioned for about a minute and had become settled and compacted. As a result of following this procedure in respect to depth of column, the weight of soil used varied from about 40 to 85 gm., depending upon the class of soil.

The maximum vacuum pressure produced by the water jet pump on the faucet was about 15 mm., and that of the high vacuum pump, about 4 mm. When the water is suctioned from the soil, however, the vacuum pressure produced by both systems is probably the same, because it is limited in both cases by the vapor pressure of the water. Although the maximum vacuum pressure may not be maintained throughout the experiment, nevertheless the pressure is high, as evidenced by the fact that great force is required to detach the Büchner funnel from the suction flask, because of the vacuum pressure in the flask.

The following three factors appear to exert the greatest influence on the results: (a) preparation of the soil sample, (b) amount of soil sample used, and (c) the compactness of the soil, but especially the last two. Whether the soil is used in lumps and allowed to slake in water into its natural ultimate texture (1) or whether it is mechanically ground fine, makes an enormous difference in the results, especially in the finer textured soils. The use of smaller samples of soils, such as 5 or 10 gm., does not yield satisfactory results. The best and most consistent results are obtained by the procedure finally adopted wherein funnels  $5 \times 2\frac{1}{2}$  cm. are filled with dry soil which is carefully broken up to pass a 2-mm. sieve, and the soil is compacted by gently tapping the lower end of the funnel against the table a few times. As a result of using larger amounts of soil and compacting it, a high suction pressure tends to maintain itself throughout the experiment.

When the procedure outlined is followed closely, the suction method, whether the water jet pump or the high vacuum pump is used, gives consistent results, duplicate tests usually agreeing within 1 per cent and rarely disagreeing more than 2 per cent.



## EXPERIMENTAL RESULTS

*Comparison between water jet pump and high vacuum pump*

In table 1 are shown the moisture equivalent data as obtained on a number of representative soils by the suction method, using for comparison both the water jet pump and the high vacuum pump. The amount of soil used ranged

TABLE 1  
*Comparison of moisture equivalent determined by use of water jet pump and high vacuum motor pump*

SOILS	MOISTURE EQUIVALENT	
	Water jet pump	Vacuum motor pump
	<i>per cent</i>	<i>per cent</i>
Michigan sand.....	5.3	4.9
Fallbrook sandy loam, 14-27½".....	12.3	12.5
Sierra Vista sandy loam, 24-43".....	12.0	12.3
Clarion loam surface.....	15.8	16.1
Bladen loam, 8-15".....	15.6	15.5
San Joaquin sandy loam, 0-14".....	11.8	12.5
Miles fine sandy loam.....	24.4	23.6
Colby silt loam, surface.....	28.0	28.1
Cecil clay loam, 1-8".....	20.5	20.9
Pierce sandy loam surface.....	27.9	27.5
Clarion silt loam, surface.....	27.7	26.9
Colby silt loam, subsoil.....	23.3	22.6
Bladen loam, 12-18".....	31.9	31.6
Decatur clay, 84".....	31.8	31.7
Antioch clay loam, 40-60".....	30.9	30.4
Kerwin fine sandy loam, 8-12".....	37.7	37.8
Lake Charles clay, surface.....	37.7	32.0
Susquahanna clay, 2-6".....	37.0	36.5
Decatur clay, 10-16".....	28.0	28.1
Clinton silt loam.....	25.1	25.5
Marion silt loam, surface.....	29.3	28.5
Haldemond clay surface.....	35.4	34.8
Hagerstown clay loam, 20-30".....	40.7	40.5
Irredel loam, 12-16".....	47.8	47.1
Copay clay adobe.....	38.6	37.9
Davidson clay loam, 9-30".....	38.7	37.8
Parson's silt loam B.....	44.1	44.4
Clyde clay.....	48.7	49.0
Webster silty clay loam, surface.....	45.7	45.1
Stockton clay adobe.....	49.1	48.5
Yolo silt loam, 1-18".....	48.3	47.6
Lufkin clay, 0-3".....	52.3	51.8
Lufkin clay, 10-16".....	62.8	61.9
Fargo clay B.....	55.3	55.0
Marengo clay 48".....	70.2	69.3
McKenzie clay, B <sub>2</sub> .....	72.2	71.8

anywhere from about 40 to 85 gm., depending on whether it was a clay or a sand soil. All soils were suctioned for about 15 minutes.

The data in table 1 show the expected variation in moisture equivalent according to the textural composition of the soil. Probably the most interesting fact revealed is the very close agreement between data obtained by use of the water jet pump and the high vacuum pump. It will be noted that the

TABLE 2

*Comparison between suction method and centrifuge method for determining moisture equivalent*

SOILS	MOISTURE EQUIVALENT		
	Suction Method Bouyoucos	Centrifuge Oskamp	Method by Middleton
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
82-7-3:			
A <sub>1</sub> .....	26.2	25.49	
A <sub>2</sub> .....	24.2	22.15	
B <sub>1</sub> .....	28.6	26.35	
C <sub>1</sub> .....	30.5	29.71	
C <sub>2</sub> .....	13.5	14.70	
132-2-23:			
A <sub>1</sub> .....	21.4	21.54	
A <sub>2</sub> .....	16.9	15.73	
B <sub>1</sub> .....	16.2	17.78	
B <sub>2</sub> .....	26.5	25.25	
OOS-1:			
C <sub>1</sub> .....	31.1	27.3	
Marengo clay 48.....	70.2	65.7	67.0
Fargo clay B.....	55.3	49.1	47.9
Fargo clay B, ground fine.....	60.1		53.2
Michigan sand.....	5.3	2.1	2.7
Haldemond clay, surface.....	35.4	31.6	32.1
Haldemond clay, surface, ground fine.....	39.2	32.9	33.8
Sierra vista sandy loam.....	12.0	10.5	8.5
McKenzie Clay, B <sub>2</sub> .....	72.2	70.1	64.2
Fallbrook sandy loam, 14½-27½".....	12.3	12.3	12.7
Colby silt loam, surface.....	28.0	27.5	27.4
Lake Charles clay, surface.....	32.2	29.7	28.7
Copay clay adobe.....	38.6	35.3	34.1
Lufkin clay, 10-16".....	62.8	58.3	56.0
Davidson clay loam, 9-30".....	38.7	36.5	33.8
Davidson clay loam, 9-30", ground fine.....	43.0		41.9

agreement is within 1 per cent. From this, it can be concluded that either vacuum system can be used for determining the moisture equivalent of soil.

*Comparison between suction method and centrifuge method*

In table 2 is presented a comparison of the moisture equivalents of various soils, as obtained by the suction method and the centrifuge method of Briggs and McLane.

The comparison in table 2 of the moisture equivalent determined by the suction method and by the centrifuge method shows that in some soils the two methods agree very closely, whereas in others the agreement is not so close. On the other hand, the results by the centrifuge method at the two different laboratories do not agree very closely in all the soils. In general, the suction method tends to give somewhat higher values than the centrifuge method. Indeed, it is rather interesting that the two methods agree as closely as they do, since in the centrifuge method the soil is centrifuged for 40 minutes at a force 1,000 times gravity, whereas in the suction method the soil is suctioned for only 15 minutes at a possible suction pressure of only about 15 mm. Since the centrifuge method is an empirical and not an absolute method and it is very sensitive to variations in technique, as shown by Veihmeyer (6), its disagreement with the suction method in some of the soils probably loses considerable of its significance. In fact, it is believed that the suction method gives a truer comparison in the moisture equivalent between heavy clays and the coarse sands than does the centrifuge method. This is because the sands present no obstacle to the free escape of water during centrifuging, whereas the heavy clays, with high colloidal content, tend to become compacted and thereby impede the rate of water escape, with the result that the sands lose proportionally more water than the clays. In the suction method the clays do not become compacted and they are never waterlocked. The idea that the centrifuge may not give a true comparison in the moisture equivalent between the heavy clays and the sands is further supported by the results of Veihmeyer (5), who found that the field capacity of some sandy soils is appreciably higher than their moisture equivalents. Furthermore, there is some evaporation loss from the soils during centrifuging. Lebedeff (4) found that the evaporation loss amounts to 3.5 per cent in a clay when centrifuged for 5 minutes at a speed equal to 70,000 times gravity. When a sand contains only 5 per cent moisture and loses even 1 per cent by evaporation, its comparison with a clay which contains 70 per cent water and loses 3.5 per cent by evaporation becomes distorted. In the suction method, there is very little evaporation, as the soil is covered with a tumbler containing a damp cloth and the suction is only for 15 minutes. Experimental data show that this loss amounts to only about 0.2 to 0.3 per cent.

Since the suction method as finally standardized is accurate, duplicate tests agree very closely, and since it gives results close to those of the centrifuge method, and since it is simple, rapid, convenient, and easily available, it would seem that it is a useful and desirable method for making a comparison of the moisture holding power of soils, especially in laboratories where the centrifuge method is not available. For comparative purposes, the suction method seems to be as reliable as the centrifuge method.

#### SUMMARY

The suction method for determining the comparative water holding power of soils, or the moisture equivalent, has been further studied and improved.

The principle of the method consists of pulling water out of the soil by suction or vacuum forces and bringing the water holding power of soils to a comparable basis.

Two different systems were used to produce the suction or vacuum forces: (a) the water jet or filter pump, and (b) the motor vacuum pump.

The method as finally standardized gives very close agreement in replicate tests.

The water jet pump gives almost exactly the same results as the motor high vacuum pump.

The suction method has been compared with the standard centrifuge method for determining moisture equivalent, and the results show that the two methods agree fairly close in the majority of soils investigated. In general, the suction method tends to give somewhat higher values than the centrifuge method.

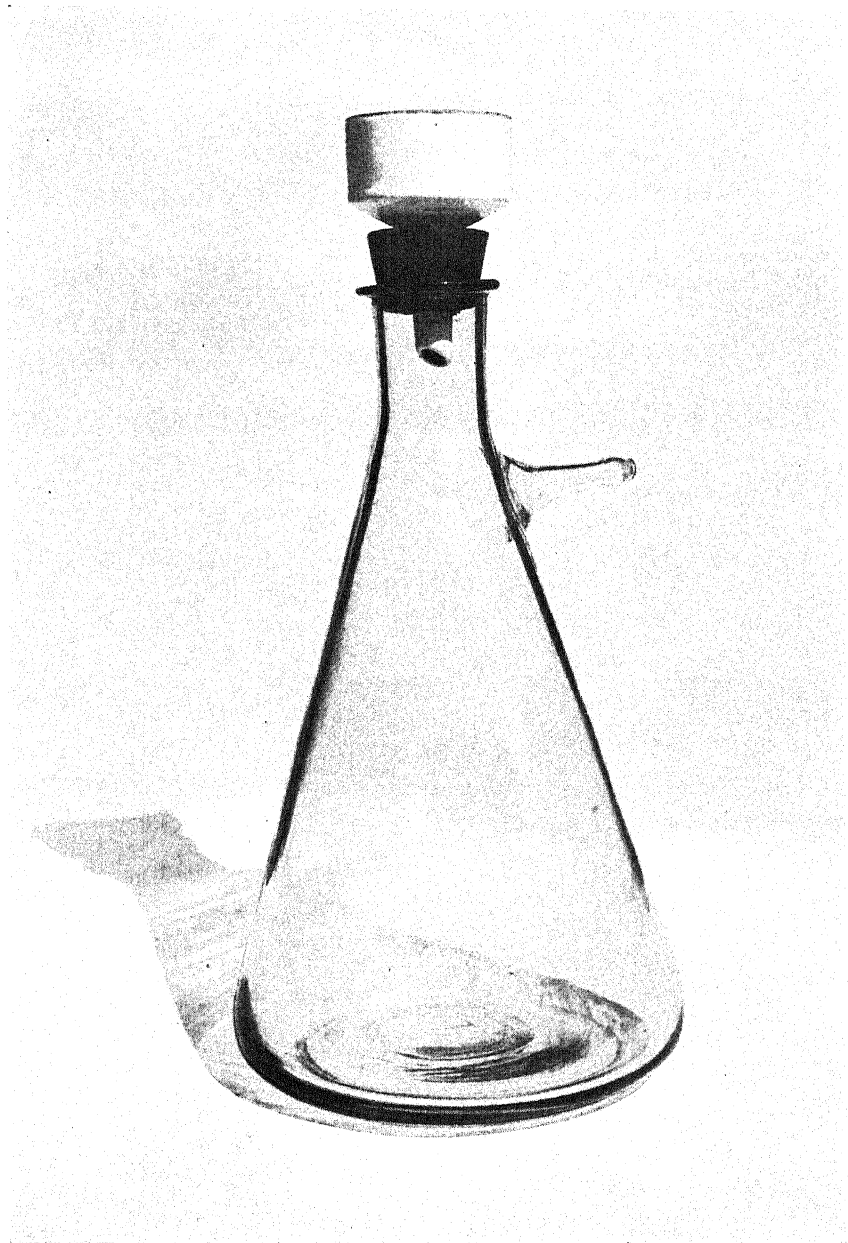
It is concluded that since both methods are empirical and give only comparative results, and since the suction method is simple, convenient, rapid, and infinitely more available, it should be of value especially to those laboratories that do not have moisture equivalent machines.

#### REFERENCES

- (1) BOUYOUCOS, G. J. 1927 The ultimate natural structure of soils. *Soil Sci.* 28: 27-37.
- (2) BOUYOUCOS, G. J. 1929 A new, simple, and rapid method for determining the moisture equivalent of soils and the rôle of soil colloids on this moisture equivalent. *Soil Sci.* 27: 233-241.
- (3) BRIGGS, LYMAN J., AND McLANE, J. W. 1907 The moisture equivalent of soils. *U. S. Dept. Agr. Bur. Soils Bul.* 45: 1-23.
- (4) LEBEDEFF, A. F. 1927 Method of determining the maximum molecular moisture holding capacity of soils. *Proc. and Papers First Internat. Cong. Soil Sci.* 1927: 551-563.
- (5) VEIHMEYER, F. J. 1931 The moisture equivalent as a measure of the field capacity of soils. *Soil Sci.* 32: 181-193.
- (6) VEIHMEYER, F. J., ISRAELSEN, O. W., AND CONRAD, J. P. 1924 The moisture equivalent as influenced by the amount of soil used in its determination. *Univ. Calif. Tech. Bul.* 16: 1-65.

#### PLATE 1

THE SUCTION METHOD FOR DETERMINING MOISTURE EQUIVALENT IN SOILS





# A MACHINE FOR THE SUBSURFACE TREATMENT OF SOILS WITH CHLOROPICRIN AND WITH CARBON BISULFIDE FOR NEMATODE CONTROL UNDER FIELD CONDITIONS

J. R. NELLER AND R. V. ALLISON

*Everglades Experiment Station, University of Florida*

Received for publication September 17, 1934

Injury to crops by the root-knot nematode (*Heterodera marioni* (Carnu) Goodey is widespread throughout the southeastern United States. Although the problem is receiving considerable attention, the amount of attention is much less than its seriousness should command. At the present time the infestation is becoming increasingly severe in the organic soils of the Everglades where the degree of susceptibility for various crops appears to be somewhat similar to that given by Watson (9) for plants in other regions of Florida. Thus tomatoes, celery, beans, peppers, peas, and other crops of high economic importance are readily attacked.

Among the various lines of approach to this problem undertaken at the Everglades Experiment Station is that of treating the infested fields with chemicals. Even though the cost of chemical treatment is rather high, still it may be feasible for the disinfection of small areas that are to be used for seedbeds. Two of the chemicals that are under trial are chloropicrin and carbon bisulfide. Of these, the latter is the more commonly used in work of this nature.

Recent work with carbon bisulfide in soil treatments has been reported by Lane and Gibson (5) for wireworm control under field conditions, and by Newhall (7) and Guba (3) for the combating of nematodes in greenhouse soils. Chapman (2), Strand (8), and others have used chloropicrin for fumigation of cereal products and household insects. It appears that the earliest use of chloropicrin for soil fumigation was made in England by Mathews (6) who applied the liquid by means of an injector designed for handling carbon bisulfide under similar circumstances. Johnson and Godfrey (4) found chloropicrin to be effective against nematodes in Hawaiian pineapple soil but experienced difficulty<sup>1</sup> with the type of injector employed by Mathews. Similar mechanical difficulties with this type of apparatus were encountered in the present instance. Moreover, the method of application is laborious.

Thus the use of carbon bisulfide and especially of chloropicrin for soil sterilization has been very seriously handicapped by lack of a suitable means of application. Recently a satisfactory method has been developed for the

<sup>1</sup> Private communication.

handling of such chemicals in subsoil treatments, at least under Everglades conditions. Although the experimental work with this machine is only preliminary, it was considered advisable to devote this paper to a discussion of the equipment and procedure in their present stage of development so that their use might be made known to others engaged in root-knot control or allied investigations under various soil conditions. The basic principle of this method suggested itself as a result of the successful use of the mole machine for water table control in the Everglades as discussed in an Annual Report (1) of the Everglades Experiment Station.

#### DESCRIPTION OF MACHINE

A general view of the experimental machine for the subsoil application of these chemicals is shown in plate 1, figure 1. Its most essential features consist of an iron pipe which is pulled through the soil in a horizontal position at a determined depth by means of a vertical cutter-bar, to which it is attached. The tube which conducts the chemical passes down behind the cutter-bar and into the horizontal pipe. Plate 1, figure 2, gives a more detailed view of the cutter-bar (A), 15 inches long, 2 inches wide, and  $\frac{1}{8}$  inch thick; and the attached pipe (B), 8 inches long and 1 inch in diameter. A second pipe of  $\frac{1}{4}$  inch diameter is contained inside the 1-inch pipe and extends up the back side of the cutter-bar, to which it is firmly brazed. A flexible hose connects this pipe with the liquid supply tank (C). The outlet for the liquid is through a small hole in a brass spray nozzle cap which is attached to the end of the inner horizontal pipe. This outlet is protected from closure by the surrounding soil by means of a pipe-union (D) which is screwed over the end of the outer 1-inch pipe. The rate of flow is varied by selection of a brass cap perforated by an orifice of the required diameter. The roller (E) compacts the soil into the opening made by the cutter-bar (A).

As shown in plate 1, figure 1, this mole and cutter-bar are pulled through the soil at a determined depth and at a constant speed by means of a tractor, in this case a 3 horse-power Bolens cultivator. Since the machine has a constant rate of movement and a constant rate of liquid ejection, the amount of material desired to be used per acre can be closely controlled. In the experimental machine (pl. 1, fig. 1) the rate of application was still further controlled over rather wide ranges by maintaining a selected pressure in the liquid supply tank, which was equipped with an air pump and a pressure gauge.

For commercial usage it is not necessary to maintain pressure in the supply tank, as the desired variations in rate of application can be obtained with sufficient accuracy by means of adjustment of the size of the orifice outlet; by the rate of movement of the machine; and by the distance between the paralleled lines of application. Furthermore the size of the machine can be varied as desired by attaching a number of units to a draw-bar which also carries the leader-pipe for the liquid conducting system. The energy required for handling the machine in muck soils has been found to be about one horse power



per unit at the draw-bar. Slightly more power was necessary in a sandy soil, however, even though it had been plowed to the desired depth of application. It is important that plowing should precede the applications in order to provide for the rapid and thorough diffusion of the chemicals through the soil.

Another essential feature, shown in plate 1, is a roller to be attached to the dispensing machine. It may also follow as a separate unit to compact the soil into the opening made by the cutter-bar, thereby checking the escape of the vaporized chemical to the air. In some cases it may also be advisable to precede the cutter-bar by a rolling coulter and thus reduce the power requirement. Such a coulter also makes it possible to reduce the width and thickness of the cutter-bar knife, thereby causing less of a soil disturbance above the liquid applications.

TABLE 1

*Conditions and results of applications of chloropicrin and of carbon bisulfide by means of the machine described*

MATERIAL	TANK PRESSURE PER SQUARE INCH	SIZE OF ORIFICE	DEPTH OF APPLICATION	DISTANCE BETWEEN LINES OF APPLICA- TION	RATE PER ACRE	INFESTATION ON OKRA PLANTED ONE WEEK LATER
	<i>pounds</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>pounds</i>	
Chloropicrin.....	5	3/64	4, 6 and 9	18	135	Severe
Chloropicrin.....	5	3/64	4, 6 and 9	12	203	Slight
Chloropicrin.....	5	3/64	4, 6 and 9	6	405	None
Carbon bisulfide.....	7	1/16	4, 6 and 9	18	302	Very severe
Carbon bisulfide.....	7	1/16	4, 6 and 9	12	453	Severe
Carbon bisulfide.....	7	1/16	4, 6 and 9	6	906	Moderate

## EXPERIMENTAL RESULTS

Table 1 records the factors that were found to be necessary for the application of chloropicrin and of carbon bisulfide at three different rates per acre for each. With chloropicrin an application rate of 135 pounds per acre was obtained with an orifice outlet  $\frac{3}{64}$  inch in diameter, a tank pressure of 5 pounds, and the lines of application 18 inches apart. Application rates of 203 and 405 pounds per acre were obtained by reducing the distance between the lines of applications to 12 and to 6 inches, respectively. Carbon bisulfide was applied at the rates of 302, 453, and 906 pounds per acre by limiting the distances between treatments to 18, 12, and 6 inches, respectively, using an orifice of  $\frac{1}{16}$  inch and a tank pressure of 7 pounds.

The lateral diffusion of the chemicals in peat was studied by planting an indicator crop of beans in parallel rows 6 inches apart, one directly over the treatment. In general, it appeared that the rows 6 inches to one side of the line of treatment were well protected whereas those 12 inches away were not. This would seem to indicate, therefore, that the lines of application should

be somewhere between 12 and 18 inches apart. Various factors such as type and condition of soil, moisture content, temperature, and severity of infestation would affect the requirements of spacing between the parallel lines of treatment for any given chemical.

The machine has been used successfully to apply chloropicrin and carbon bisulfide at rates varying from 135 to 906 pounds per acre at depths of 4, 6, and 9 inches (table 1). It may be used with any free-flowing liquid or for a combination of liquids prior to, or subsequent to, their arrival under the soil surface. In the latter case two parallel pipes from each of two supply tanks would need to be led down the cutter-bar and into the underground pipe core. Otherwise the ground would have to be gone over twice with a different liquid in the machine each time.

In the case of chloropicrin, the supply tank may be filled and the rate of flow calibrated out of doors with little discomfort if one keeps on the windward side and somewhat above the exposed liquid. The rate of flow is conveniently determined by measuring the amount of liquid that is ejected in a given number of seconds. This factor, together with a knowledge of the speed of the machine, permits a calculation of the amount used per acre for any given spacing between lines of treatment.

When applying chloropicrin it is well to close the outlet valve just before elevating the cutter-bar out of the soil. Preliminary experiments have indicated that the liquid should be liberated at a depth of about 6 inches below the soil surface. In these trials in a peaty soil additional benefits have not been obtained by covering the soil with mulch paper following the applications of the material and the compacting action of the roller.

The experiments were conducted in a field so badly infested with nematodes that susceptible crops such as celery and beans could no longer be grown. No root knot was observed on an indicator crop of okra on the plots treated with chloropicrin at the rate of 405 pounds per acre. There was some infestation where the treatment was at the rate of 203 pounds per acre (table 1), while on the check plots the plants were killed by the root knot. It is believed that the amount of chloropicrin required can be materially reduced by maintaining a thoroughly clean fallow condition in the soil for a longer time before the applications are made. This period of clean fallow should be sufficiently long to insure the complete rotting and disintegration of the root masses, otherwise they will offer sufficient protection to the nematode population harbored in them to defeat the sterilizing effect of the chemical.

Only those chemicals can be used that have a transient existence in the soil, for as long as a chemical is toxic to the nematode it is very likely to be toxic also to plant growth. For this reason the importance of having the root masses well rotted cannot be over emphasized. All weed growth should be avoided also, as some of the common weeds are active hosts for root-knot organisms. It is possible that a crop not susceptible to root knot may be grown during this period of preparation for chemical treatment, but it is not known that this point has been verified experimentally.

Preliminary experiments have indicated (table 1) that over three times as much carbon bisulfide as chloropicrin is necessary for an equal control of the nematode *H. Marioni*. In addition, because of its fire and explosive hazard by either free flame or by friction, carbon bisulfide is inconvenient to handle. Because of its high vapor pressure, carbon bisulfide in an air-tight container should not be left exposed to the heating effects of the sun's rays. Such an exposure tended to cause the pressure in the supply tank of the dispensing machine (pl. 1, Fig. 1), even though painted white, to be materially increased above that required for the desired rate of flow. The effect was largely prevented by keeping the tank covered with wet burlap bags.

Either chloropicrin or carbon bisulfide is suitable from the standpoint of after effects in the soil, as plants grew normally when seeded within about a week after the treatments. In view of the particularly favorable results with chloropicrin it is to be hoped that a quantity demand for it for soil sterilization purposes will reduce its cost to a point where it may be economically possible to use it on a field scale larger than small seedbed areas.

In the case of the truck crops that are transplanted from seedbeds it is vital that the young plants should be free from root knot, for the reason that a plant already affected by an actively developing disease has less chance for normal growth when placed either in a clean or in an infested field. It is in the sterilization of seedbeds, therefore, that chloropicrin probably will be used first, and the dispensing machine described is well adapted for such usage.

It is obvious, also, that other solutions may be distributed by this type of equipment in the combating of other soil infestations whether of a fungous or an insect character.

#### SUMMARY

A machine based upon the mole principle has been developed whereby chloropicrin and other disinfecting liquids may be applied in a continuous manner beneath the soil surface. The rate of flow is calibrated from a knowledge of the speed of the equipment and of the amount of liquid ejected per unit of time. Chloropicrin can be applied conveniently by this means and was found more effective than carbon bisulfide in controlling the root knot nematode *Heterodera Marioni* in peat land as measured by the development of crops that are highly susceptible to attacks by the organism.

#### REFERENCES

- (1) ALLISON, R. V. 1928 *Ann. Rpt. Univ. Fla. Agr. Exp. Sta.* 1928: 118.
- (2) CHAPMAN, R. N. 1925 Possibilities and limitations of chloropicrin as a fumigant for cereal products. *Jour. Agr. Res.* 31: 745-760.
- (3) GUBA, E. F. 1932 Carbon disulfide emulsion for the control of the root-knot nematode. *Mass. Agr. Exp. Sta. Bul.* 292.
- (4) JOHNSON, M. O., AND GODFREY, G. H. 1932 Chloropicrin for nematode control. *Indus. and Engin. Chem.* 24: 311-313.

- (5) LANE, M. C., AND GIBSON, K. E. 1932 Carbon disulfide as a control for wireworms. *Jour. Econ. Ent.* 25: 958-967.
- (6) MATHEWS, D. J. 1930 Sixth Ann. Rpt. Exp. Res. Sta. Nursery Market Garden Industries, Dev. Soc. Ltd., Turners Hill Chesnut, Herts.
- (7) NEWHALL, A. G. 1930 Control of root-knot nematode in greenhouses. Ohio Agr. Exp. Sta. Bul. 451.
- (8) STRAND, A. L. 1927 A comparison of the toxicity and the diffusion in a column of grain of chloropicrin, carbon disulfide and carbon tetrachloride. Minn. Agr. Exp. Sta. Tech. Bul. 49.
- (9) WATSON, J. R. 1929 The control of root-knot in seedbeds. Fla. Agr. Exp. Sta. Press Bul. 416.

#### PLATE 1

FIG. 1. General view of the experimental machine showing the liquid supply tank and hose connection with the pipe leading to the subsurface outlet.

FIG. 2. Detail of the dispensing system showing the cutterbar (A), the horizontal subsurface outlet pipe (B), the liquid control valve (C), and the pipe union (D) to protect the orifice outlet from clogging. E is the compacting roller.

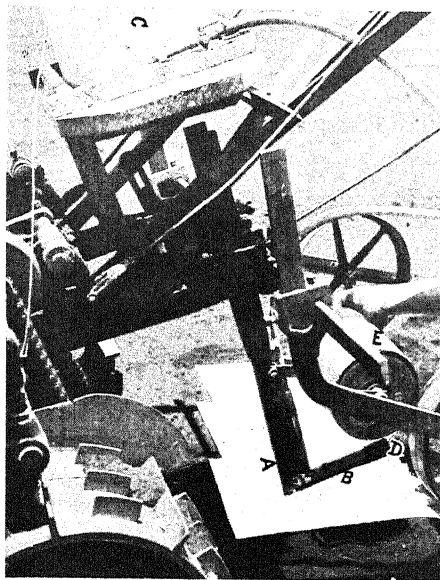


FIG. 1

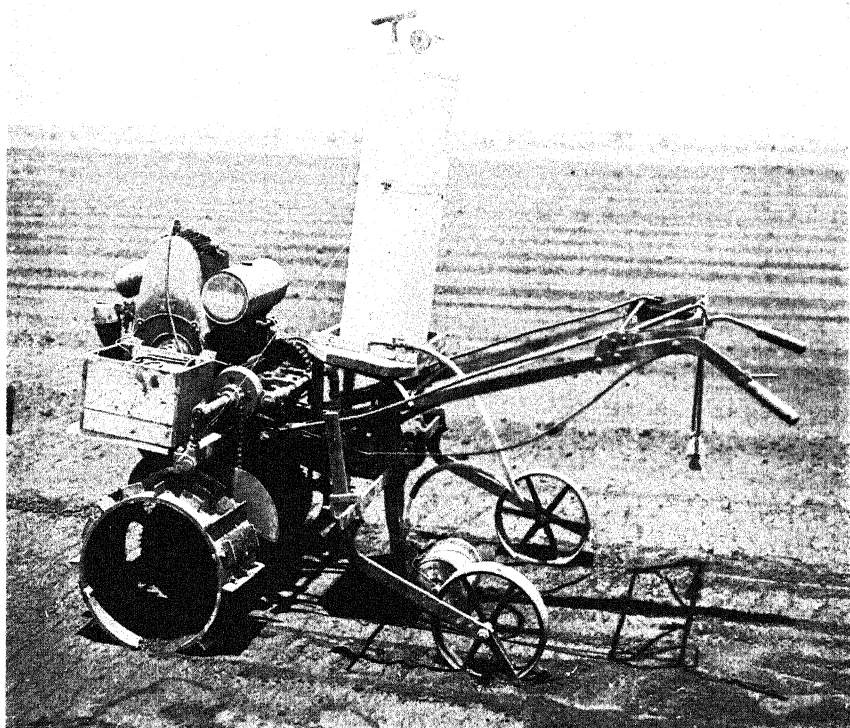


FIG. 2



# A COMPARATIVE STUDY OF THE BACTERIAL FLORA OF WIND-BLOWN SOIL: VI. DEATH VALLEY, CALIFORNIA, WITH SUMMARY OF SIX SOIL STUDIES

LAETITIA M. SNOW

*Wellesley College*

Received for publication August 8, 1934

On February 2, 1933, sand was collected from north and west faces of a bare dune in the northern part of Death Valley.<sup>1</sup> As exceedingly dry sand was anticipated, apparatus for collecting at different depths was not brought, consequently the soil was collected with sterile instruments at approximately 6 inches, the sand scraped away to the 12-inch level, and more sand collected. This was repeated for the 24-inch level, the whole collection being placed in a single container. The 6-inch layer was quite dry, but totally unexpected was the damp condition of the 12-inch and 24-inch layers, due to a storm 10 days previous. The can containing the sand was kept out of doors overnight and carried to Long Beach the next morning by motor and train. It was stored in the vegetable compartment of a Frigidaire overnight and plated the next morning at the University of California at Los Angeles, in Difco nutrient agar, 6 plates each at 1:100, 1:1,000, and 1:10,000 dilutions.

The count was made after incubation at room temperature for 9 days. One hundred colonies were streaked on agar, stored at room temperature for approximately 2 weeks, after which they were carried to the Hopkins Marine Station of Stanford University at Pacific Grove, California, for further study. The methods used in the study of the soil were identical with those of previous studies (18, 19, 20, 21, 22). Nitrate, sucrose, and lactose agar were used instead of broths, and glucose agar was used instead of glucose gelatin, on account of the difficulty in detecting small amounts of acid in glucose gelatin.

## CHARACTER OF THE SOILS

Death Valley sand was very fine and uniform in size of grains. All but a few tiny grains passed through the 0.589-mm. sieve of a Tyler Standard Screen

<sup>1</sup> The collection of sand in Death Valley was made possible by the courtesy and assistance of Miss McHendry and Mr. Stacy, Hunter-Clarkson courier and driver, to whom my sincere thanks are presented. I wish also to express my thanks to Prof. T. D. Beckwith of the department of bacteriology of the University of California at Los Angeles, and his assistant, Miss Kosht, who most kindly lent apparatus and furnished media and laboratory facilities, without which the work would not have been possible. As the greater part of the study was carried on at the Hopkins Marine Station of Stanford University at Pacific Grove, California, I wish to present my sincere thanks to Director W. K. Fisher for the courtesy extended to me, and especially to Dr. C. B. van Niel, in whose laboratory the work was done.

Scale, approximately 1 per cent remained on the 0.295-mm. sieve, 92.41 per cent remained on the 0.104-mm. mesh, and the remaining 6.42 per cent passed through the latter.

TABLE 1  
*Precipitation and temperatures for 5 years previous to study (23, 24, 25, 26, 27)*

SECTION	LOCALITY	PRECIPITATION		TEMPERATURES	
		Average annual	Variation	Average mean annual	Variation
		<i>inches</i>	<i>inches</i>	<i>°F.</i>	<i>°F.</i>
Fresh water.....	Hobart, Ind.	33.10	28.72-38.20	50.06	-20-102
Atlantic coast.....	Provincetown, Mass.*	37.95	32.88-42.61	47.10	2- 91
	Beaufort, N. C.	54.83	40.70-73.26	63.96	13- 96
Pacific coast.....	Del Monte, Salinas, Cal.	11.69	7.21-16.06	55.60	24- 95
Inland.....	Univ. Arizona, Tucson, Ariz.*	12.20	9.12-18.01	66.50	1-111
	Greenland Ranch Death Valley, Cal.	0.39	0.00- 0.57	75.80†	18-126

\* In making a comparative study of the climatological data the reports for these stations seemed more nearly complete than those used in previous reports (18, 19).

† Given for 1929 only.

TABLE 2  
*Physical character of the six soils*

LOCALITY	SIZES OF PARTICLES		WATER CONTENT	WATER CAPACITY	OPTIMUM WATER CONTENT*	RELATIVE WATER CONTENT†	COMBUSTIBLE MATERIAL
	>0.5 mm.±	0.1-0.5 mm.±					
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Lake Michigan.....	0.77	98.86	2.85	25.00	17.50	10.72	0.33
N. Atlantic.....	73.94	25.80	2.87	23.50	16.45	12.21	0.27
S. Atlantic.....	13.40	51.10	2.31	23.00	16.10	10.04	0.45
Pacific.....	0.49	99.31	2.70	23.69	16.58	11.49	0.07
Arizona.....	4.19	45.00	2.01	27.70	19.37	7.30	1.90
Death Valley.....	0.00±	93.38	2.14	29.50	20.65	7.21	0.27‡

\* 70 per cent of capacity.

† Percentage of optimum water content present.

‡ On account of a misunderstanding, the combustible material was not burned off until February 7, 1934; during the interval the soil had been kept in a sealed box.

In attempting to compare the physical characters of the six soils, there is some difficulty in finding correlations with the climatic conditions. The Atlantic soils are coarser and have a water content nearer the optimum, and the regions have a higher rainfall than the others, which are inconstant in their order. It is evident that the climates of the two arid areas are most nearly alike. The north and south Atlantic areas are also similar, with the Pacific



area coming in between these two groups. The lake station holds an independent position, having rainfall similar to the north Atlantic, an annual mean temperature between the north Atlantic and the Pacific coast, and the greatest temperature range of all the stations.

From table 3 it is evident that the two desert soils agree in pH and high salt content. Death Valley, long noted for the salt accumulation in its soil, heads the list for total salts, which are predominately chlorides, nitrates, etc.

TABLE 3  
*Chemical character of the six soils*

LOCALITY	REACTION	TOTAL SOLUBLE SALTS	CO <sub>2</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub> ETC.
	<i>pH</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Lake Michigan.....	7.5-8.0	0.0120	0.0005	0.0082	0.0005	0.0028
N. Atlantic.....	6.8-7.2	0.0070	0.0050	Trace	Trace	0.0020
S. Atlantic.....	9.0-9.2	0.0107	0.0059	0.0016	0.0006	0.0028
Pacific.....	5.9-6.1	0.0045	0.0014	0.0005	0.0008	0.0018
Arizona.....	8.6-9.0	0.0540	0.0100	0.0120	0.0010	0.0350
Death Valley*.....	8.9-9.0	0.4377	0.0132	0.0383	0.1989	0.1872

\* The reaction was very kindly determined by Dr. C. B. van Niel, and the chemical analysis was made by Miss Miriam Dice, the analyst for four of the other samples.

TABLE 4  
*Average total numbers of organisms and percentages of kinds in the six soils*  
(Per gram of fresh soil)

LOCALITY	DATE OF COLLECTION	TOTAL COUNT	BACTERIA OR YEASTS	ACTINO- MYCETES	FUNGI
			<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Lake Michigan.....	June 27, July 4	17,600	82.80	15.19	2.00
N. Atlantic.....	September 12	93,700	73.53	24.01	2.56
S. Atlantic.....	March 30	59,666	99.12	0.61	0.27
Pacific*.....	July 8, October 10	60,346	53.79	44.72	1.47
Arizona.....	April 18	1,072,000	46.81	52.40	0.77
Death Valley.....	February 2	17,800	89.32	10.11	0.56

\* Averaged for the two collections.

It also has the highest carbonate content of the six soils. Arizona follows, but with noticeably low chlorine content and high percentage of nitrates, etc. The two Atlantic soils are closely alike except for the pH, which is difficult to explain from the figures given. The Pacific sand was the only acid soil studied; it had more CO<sub>2</sub> than the Lake Michigan sand but was noticeably lacking in soluble salts. In appearance it seemed to be almost pure silica sand.

On the assumption that 21°C. and evenness of temperature, moderately fine

soil grains (0.1–0.5 mm.), optimum water content, abundance of rain, pH 7, combustible material, and low soluble salt content are favorable factors, the soils were graded on these characters and the numbers were added; the lowest indicating the most favorable conditions. From these grades the stations arrange themselves in the following order: north Atlantic 22, south Atlantic 23, Pacific 24, Lake Michigan 28, Arizona 30, and Death Valley 36.

#### PLATE COUNTS

The plates of Death Valley soil were counted first without a lens, bacterial colonies checked with a hand lens, and actinomycetes with a 16-mm. objective. The numbers on the 1:10,000 dilution plates were too few to be accurate and were therefore not included in the results.

From tables 1, 2, 3, and 4 there seems to be no clear correlation between the environmental factors and the total number of organisms nor between the proportions of the various kinds. The two arid regions are nearly at the two ends of the series as to numbers. The region with the highest annual rainfall (S. Atlantic) has a total count very close to a region (Pacific) with only 11.59 inches per annum. How far this lack may be compensated for by the Pacific fogs cannot be stated.

The results of Khalil's work (15) showed that drying reduced numbers but that dried soil moistened had higher numbers than permanently moist soil, due to better availability of organic matter. This suggests a reason for the high count in Arizona, which had also a comparatively high percentage of combustible material. The low number in Death Valley is not entirely an exception to this correlation, since this soil had little organic matter.

The proportion of fungi appears to follow, not climatic factors, but rather roughly the pH. Arizona, Death Valley, and south Atlantic soils all are poor in fungi and have high pH values. The highest count for fungi, however, is not in the most acid soil (Pacific) but in the one most near neutrality (north Atlantic). The high counts for actinomycetes were in the Pacific and Arizona soils, which were dry but not the driest, one acid and one basic. The lowest count for this group was in a basic soil (south Atlantic) which had the highest rainfall of the series. If low rainfall were solely responsible for high numbers, however, north Atlantic soil should not have approximately 9 per cent more actinomycetes than Lake Michigan soil. Jensen (13) is of the opinion that pH, except for highly acid soils, has no effect on numbers of actinomycetes, and gives, in his second paper (14), pH 5–6 as the critical point. This would make the Pacific soil just at the critical point, but not below it. Death Valley and Lake Michigan soils have approximately the same percentage of actinomycetes as was found by Brown and Benton (1) for Iowa (12.45 per cent) although the conditions in the three habitats are quite different. It is not possible to compare Dixon's results (4, 5) as her media were purposely made acid (pH 4.6) to cut down the bacteria on her plates.

## SEASONAL VARIATIONS

In discussing numbers of bacteria and climate it must not escape notice that, although an attempt was made in each case to get representative samples of soil, these collections were made usually only once and at different seasons of the year. There seems to be a great difference of opinion regarding the peak, or peaks, in the curve of yearly variation in numbers of soil organisms, due undoubtedly to the fact that many different factors entered into the different experiments.

Waksman (28) found that the peaks varied with the type of soil and the depth, and did not correlate with moisture. Cutler, et al. (3) found a maximum in November, a minimum in February or March, and a secondary peak at the end of June. These did not correlate with seasonal changes in soil moisture, rainfall, or soil temperature. Erdman (7) found that the peaks in two years were not the same; in one year there was a low in February or March, in the other, a second peak in these months. The maximum for both years was in June, and the minimum in August. These did not correlate with water content. Brown and Halversen (2), working with cropped and fallow land, found a great difference in the curves and concluded that factors other than seasonal ones controlled the numbers. Fehér (9, 10, 11) found that in pine woods and underbrush the peak came in July, whereas in Robinia steppe forest it came in September, this habitat being too hot and dry in July for the best development of organisms. The minima were in January or February. He considers (12) rainfall not so important as temperature but speaks of the complicated interaction of factors, which is evident from a study of his curves. The peaks of Rivas' curves (17) were in September or October, with the low point in November in nine cases and in February in one. Secondary peaks came in April or March. On the whole, his curves seem to correlate with those for temperature.

Fabricius and Feilitzen (8) claim that numbers agree with soil temperature, but the figures seem much too irregular for such a correlation. A similar correlation is indicated by Fehér (9) in attributing the maximum to the energy to the sun, as against rainfall or reaction of soil. On the other hand, Dixon (4, 5) considers rainfall before collection of more influence than temperature. Her work, done in Australia, reverses the seasons, and was not for complete years. Contrary to her claim, Newton (16) found three peaks between May and October, two corresponding to low and one to high moisture.

Considering the times of collection of the six soils herein reported, we find that February, which seems to have given more minima than maxima, may be a factor in the low count of Death Valley sand, but seasonal variation could not alone account for the low count in Lake Michigan soil, since no minima, but almost universally maxima, have been reported for June and July. April has been reported for a maximum in one case and this for cropped soil (2), which is difficult to correlate with the high count in Arizona.

## COLORED FORMS APPEARING IN THE SIX SOILS

Colors would seem to correlate more closely with chemical than with physical factors but a study of tables 3 and 5 does not reveal any close relation between the various colors and the pH or proportions of the various soluble salts. The only apparent relation seems to be the almost total lack of colored forms in the acid sand from the Pacific coast, which is poor in soluble salts, as contrasted with the results from Death Valley, which has the highest percentage of soluble salts, high pH, and the highest percentage of colored forms. There seems to be no correlation in the intermediate soils between color and total salts nor the proportions of the individual salts tested.

The high percentage of fluorescent forms in Death Valley is very interesting. At one time it was suggested that the high percentages of such forms in Lake Michigan and north Atlantic soils might be due to the proximity of large bodies of water, as contrasted with the low numbers in Arizona (20). But the low figures for south Atlantic, the almost total lack of such forms in Pacific sand

TABLE 5  
*Percentages of colored colonies on plates of six soils*

LOCALITY	TOTAL NUMBER	WHITE	YELLOW	ORANGE	RED	FLUORES- CENT	BROWN
Lake Michigan.....	1,107	83.01	3.07	0.27	0.54	13.09	Few
N. Atlantic.....	318	75.78	7.23	1.57	0.94	14.46	Few
S. Atlantic.....	1,210	83.17	8.22	0.49	0.70	7.42	0.00
Pacific.....	3,850	99.14	0.54	0.10	0.00	0.21	0.00
Arizona.....	360	88.33	6.39	0.28	1.11	1.39	2.50
Death Valley.....	1,028	57.10	14.10	1.84	0.39	26.46	0.09

and the very high numbers in Death Valley would be a direct argument against this suggestion.

## MORPHOLOGY AND PHYSIOLOGY OF SELECTED CULTURES

The 100 cultures isolated from Death Valley plates were tested for purity by repeated plating. In some cases this proved a difficult process, as two kinds of colonies continued to appear on the plates. After a long series of plates it was decided that the mucoid colonies with the wavy edges and the rough colonies with granular edges were merely two types of the same form. The cultures were not identified, but some of them agreed with the description and photographs of the two types of *B. mycoides* reported by Dooren de Jong (6), who discusses pleomorphism in this form and cites other references on the subject. About 20 other cultures continued to offer difficulties in purification until the end of the work, and as there was a question regarding their condition these forms have been omitted from this report.

In compiling table 6 the slides of the previous work were restudied in the light of subsequent study. In some cases forms previously assigned to yeasts were

thought to be more fittingly placed among pleomorphic bacteria. This rearrangement will alter the percentages slightly but will give a more correct comparison. With the exception of the California soils the percentage of gram-positive forms is fairly uniform. The south Atlantic soil stands out rather conspicuously in morphological peculiarities. The high percentage of coccus,

TABLE 6

*Morphology of cultures picked for study in six soils*

LOCALITY	TOTAL NUMBER	COCCUS OR COCCOID	PLEO- MORPHIC FORMS	NON-PLEO RODS		YEASTS	GRAM'S STAIN			
				Spores	No spores		Total num- ber	+	Vari- able	—
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Lake Michigan....	102	13.72	10.78	19.60	53.92	1.96	89	31.81	3.40	64.77
N. Atlantic.....	76	22.36	18.43	15.79	42.10	1.31	61	38.33	1.67	60.00
S. Atlantic.....	119	31.10	26.90	0.80	41.20	0.00	119	23.60	9.20	67.20
Pacific.....	92	11.96	6.52	14.12	65.21	2.17	92	56.52	0.00	43.48
Arizona.....	60	21.67	8.33	38.33	30.00	1.67	54	35.20	0.00	64.80
Death Valley.....	78	12.82	5.12	33.33	48.72	0.00	78	56.41	14.10	29.49

TABLE 7

*Physiological characters of organisms from six soils*

LOCALITY	NUMBER	FERMENTERS OF				DIGESTERS OF		REDUCERS OF NITRATES
		Glucose only	Glucose Sucrose	Glucose Lactose	Three sugars	Gelatin	Casein	
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
Lake Michigan*.....	79	7.59	17.72	0.00	3.79	70.83	32.05	18.98
N. Atlantic*.....	61	6.56	19.67	0.00	1.64	59.61	40.00	23.73
S. Atlantic.....	119	8.40	16.80	0.84	0.00	52.90	26.50	44.60†
Pacific.....	92	8.69	18.48	4.34	20.65‡	36.95	33.69	20.65
Arizona*.....	49	8.17	18.37	0.00	2.04	72.55	56.52	30.43
Death Valley.....	78	11.54	41.03	7.69	21.79	55.13	.....§	30.77

\* These tests were not all made at the same time, hence the number of cultures tested differed. In each case the percentages are made from the number tested.

† 7.5 per cent made no growth.

‡ Of this group one culture formed gas in glucose and sucrose but not in lactose. With the exception of the peculiar form noted in the report on south Atlantic soil (21) this was the only instance of gas formation in the whole series.

§ Not tested.

or coccoid, pleomorphic, and gram-negative forms, the total lack of yeasts, and the almost total absence of spore-formers are noteworthy. As the habitat is one of the most favorable of the series, these peculiarities cannot be due to rigorous conditions. Death Valley, standing at the other end of the habitat series, also lacked yeasts, but showed a very high percentage of spore-formers.

This latter characteristic might be due to the difficult conditions for life and is probably to be expected in arid soil. On the other hand, the lack of spore-formers in the south Atlantic sand cannot be due solely to favorable conditions, since the north Atlantic sand, with similarly favorable conditions for life, contained approximately 15 per cent of spore-formers. The presence of water-insoluble carbonates, which has been commented upon in another place (21), may be an important factor.

Although the high percentage of spore-formers was to be expected in arid soils, the surprising point is the relatively large numbers of non-spore-formers that can endure the conditions, presumably severe for bacteria, which exist in these areas.

The great fermentative activity of the Death Valley forms is to be noted in table 7. This does not appear to be due to habitat conditions, however, since Arizona forms agree, not with those from Death Valley, but with Atlantic and Lake Michigan cultures. Protein digesters are fairly low in Death Valley, but high in Arizona. The rather high percentage of nitrate reducers in arid soils might correlate with the high percentage of these salts were it not for the fact that the highest percentage of these forms appeared in south Atlantic soil, which contained the same percentage of these salts as did Lake Michigan sand which showed the lowest percentage of reducers.

#### NITROGEN FIXATION

At the beginning of the work an attempt was made to isolate *Azotobacter* from Death Valley soil. Two sets of flasks containing nitrogen-free media were set up, one with sodium molybdate and the other without. One of each set was placed in the window on a warm plate and one in the dark at 25°C. After 3 to 4 days a film started to form on the bottom of the molybdate flask in the light. At the end of 3 weeks additional soil was added to the flasks to hasten growth, which resulted at the end of 6 weeks in a very heavy bottom film and a thin, paraffin-like film on the surface of the molybdate flask in the light, the liquid becoming cloudy. That in the dark, and those without molybdate had no surface film and the latter group no clearly discernable film of any kind; the liquid remained clear.

Microscopic examination showed no *Azotobacter* cells, but abundant spore-formers. Cultures were streaked off and brought to Wellesley in order to test their ability to fix nitrogen. These cultures were exceedingly difficult to purify. It was also difficult to find, after several months' culture, a suitable medium on which to obtain sufficient growth for the test. In a few cultures, however, tested by the micro-Kjeldahl method, there seemed to be a very small amount of nitrogen fixed.<sup>2</sup> The writer hopes to be able to continue this work.

<sup>2</sup> This work was done by a senior, Edith Levy Elsas. The nitrogen fixation test was made in the Chemical Laboratory of Wellesley College under the direction of Associate Professor Ruth Johnstin.

## SUMMARY

Data from drifting sand collected in Death Valley, California, are compared with similar data from sand collected in the following localities: Arroyo bank, near Tucson, Arizona; dunes at Sandwich, Massachusetts; south shore of Lake Michigan, Indiana; Shackleford Bank, Beaufort, North Carolina; and the Pacific side of the Monterey Peninsula, California. These data have been published, but in some instances have been revised and rearranged for purposes of comparison.

It was not possible to find clear correlation between conditions of habitat and bacterial numbers or activity except possibly in the case of colored forms, which were almost totally lacking in the acid, salts-poor sand of the Monterey Peninsula and exceedingly abundant in the basic, salt-impregnated soil of Death Valley.

Death Valley has the driest, hottest climate of the series and fine-grained, very dry soil with pH 9 and a large amount of soluble salts.

The plate count was low, 10 per cent of which were actinomycetes. A few fungi appeared. A great abundance of colored forms appeared, with fluorescent colonies the most abundant, followed by yellow.

One third of the cultures selected for study were spore-formers and approximately one-half were gram positive. No yeasts, but a small percentage of pleomorphic forms, were found.

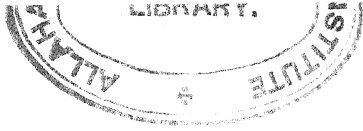
Great fermentative activity was evident, with average amount of protein digestion and nitrate reduction. No *Azotobacter* was found.

## REFERENCES

- (1) BROWN, P. E., AND BENTON, T. H. 1927 Microörganisms in some soil profiles in Iowa. *Proc. First Internatl. Cong. Soil Sci.* 3: 100-106.
- (2) BROWN, P. E., AND HALVERSEN, W. V. 1919 Effect of seasonal conditions and soil treatment on bacteria and molds in soil. *Iowa Agr. Exp. Sta. Res. Bul.* 56: 251-278.
- (3) CUTLER, D. WARD, CRUMP, LETTICE M., AND SANDON, H. 1922 A quantitative investigation of the bacterial and protozoan population of the soil with an account of the protozoan fauna. *Royal Soc. [London] Phil. Trans. Ser. B.* 211: 317-350.
- (4) DIXON, D. 1928 The microörganisms of cultivated and bush soils of Victoria. *Aust. Jour. Exp. Biol. and Med. Sci.* 5: 223-232.
- (5) DIXON, D. 1930 The microörganisms of the tertiary red sands near Melbourne, Victoria. *Aust. Jour. Exp. Biol. and Med. Sci.* 7: 161-169.
- (6) DOOREN DE JONG, L. E. DEN 1933 Ueber *Bacillus mycoides* und den Pleomorphismus. *Arch. Mikrobiol.* 4 (1): 36-53.
- (7) ERDMAN, L. W. 1928 The numbers of microörganisms in Carrington Loam as influenced by different soil treatments. *Iowa Agr. Exp. Sta. Res. Bul.* 109: 233-258.
- (8) FABRICIUS, OTTO, UND VON FEILITZEN, H. 1905 Ueber den Gehalt an Bakterien in jungfräulichem und kultiviertem Hochmoorboden auf dem Versuchsfelde des Schwedischen Moorkulturvereins bei Flahult. *Centbl. Bakt.* (II) 14: 161-168.
- (9) FEHÉR, D. 1929 Untersuchungen über den zeitlichen Verlauf der Bodenatmung und der Mikrobentätigkeit des Waldbodens. *Biochem. Ztschr.* 206: 416-435.

- (10) FEHÉR, D. 1929 Untersuchungen über den N-Stoffwechsel des Waldbodens. *Biochem. Ztschr.* 207: 350-360.
- (11) FEHÉR, D. 1930 Mikrobiologische Untersuchungen über den Stickstoff-Kreislauf des Waldbodens. *Arch. Mikrobiol.* 1: 381-417.
- (12) FEHÉR, D. 1930 Untersuchungen über den zeitlichen Verlauf der Mikrobentätigkeit im Waldboden. *Arch. Mikrobiol.* 1: 464-492.
- (13) JENSEN, H. L. 1930 Actinomycetes in Danish soils. *Soil Sci.* 30: 59-77.
- (14) JENSEN, H. L. 1931 The fungus flora of the soil. *Soil Sci.* 31: 123-158.
- (15) KHALIL, F. 1929 The effect of drying on the microbiological processes in soils. *Centbl. Bakt.* (II) 79: 93-107.
- (16) NEWTON, J. D. 1930 Season fluctuations in numbers of microorganisms and nitrate nitrogen in an Alberta soil. *Sci. Agr.* 10: 361-368.
- (17) RIVAS, D. 1911 Bacteria and other fungi in relation to the soil. *Contrib. Bot. Lab. Univ. Penn.* 3: 243-274.
- (18) SNOW, LAETITIA M. 1926 A comparative study of the bacterial flora of wind-blown soil: I. Arroyo bank soil, Tucson, Arizona. *Soil Sci.* 21: 143-161.
- (19) SNOW, LAETITIA M. 1927 A comparative study of the bacterial flora of wind-blown soil: II. Atlantic Coast sand dunes, Sandwich, Massachusetts. *Soil Sci.* 24: 39-48.
- (20) SNOW, LAETITIA M. 1927 A comparative study of the bacterial flora of wind-blown soil: III. Lake Michigan sand dunes, Indiana. *Soil Sci.* 24: 335-342.
- (21) SNOW, LAETITIA M. 1935 A comparative study of the bacterial flora of wind-blown soil: IV. Shackleford Bank, North Carolina. *Soil Sci.* 39: 227-231.
- (22) SNOW, LAETITIA M. 1935 A comparative study of the bacterial flora of wind-blown soil: V. Monterey Peninsula, California. *Soil Sci.* 39: 233-236.
- (23) U. S. Dept. Agr., Weather Bureau. Climatological Data, Arizona Section. 1918-1922.
- (24) U. S. Dept. Agr., Weather Bureau. Climatological Data, New England Section. 1920-1924.
- (25) U. S. Dept. Agr., Weather Bureau. Climatological Data, Indiana Section. 1920-1924.
- (26) U. S. Dept. Agr., Weather Bureau. Climatological Data, North Carolina Section. 1926-1930.
- (27) U. S. Dept. Agr., Weather Bureau. Climatological Data, California Section. 1928-1932.
- (28) WAKSMAN, S. A. 1916 Bacterial numbers in soils at different depths and in different seasons of the year. *Soil Sci.* 1: 363-380.





# PHOSPHATE FIXATION IN SOILS, PARTICULARLY AS INFLUENCED BY ORGANIC MATTER<sup>1</sup>

J. L. DOUGHTY<sup>2</sup>

*University of Wisconsin*

Received for publication September 22, 1934

Although soil organic matter-phosphate relationships have received much attention, a review of the literature reveals the existence of very little definite information regarding the influence of soil organic matter on the fixation of phosphate in difficultly available form. A study of this latter phase of the subject was therefore undertaken covering the following points: (a) the effect of leaching a soil with an acid or a base on its fixing power; (b) the fixation of phosphate by natural and synthetic humus material; (c) the effect of oxidizing the organic matter with hydrogen peroxide or by ignition on its fixing power; (d) the effect of heat on the solubility of iron and aluminum phosphates in 0.002 *N* H<sub>2</sub>SO<sub>4</sub>.

## METHODS AND MATERIALS

In this report the term "fixed phosphorus" is used to designate that portion of the applied water-soluble phosphate which is not recovered by extracting 1 gm. of soil with 200 cc. of 0.002 *N* H<sub>2</sub>SO<sub>4</sub> buffered to pH 3 with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. This is the extracting solution used by Truog (13) for the determination of readily available phosphorus and will be referred to as the "standard extracting solution."

The fixing power of the different materials was determined as follows: Weighed samples were placed in evaporating dishes and moistened with water, and the desired amount of monobasic potassium phosphate was added in solution. After drying on the steam bath, the samples were transferred to bottles and the standard extracting solution was added. The suspensions were shaken for 30 minutes on an end-over-end shaker and then filtered. Filtrates colored with organic matter were evaporated with magnesium nitrate and the residue ignited before the phosphorus was determined.

All phosphorus determinations were made by the Denigès colorimetric method as outlined by Truog and Meyer (14). The amount of phosphorus

<sup>1</sup> Part of a thesis submitted to the faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of doctor of philosophy. Published with the permission of the director of the Wisconsin Agricultural Experiment Station.

<sup>2</sup> The writer wishes to express his appreciation for the advice and criticisms tendered by Prof. E. Truog.

fixed was computed by subtracting the amount extracted from the treated sample from the sum of what was added to and originally present in soluble form in the sample. Phosphorus is reported in all cases as parts per million on the basis of the weight of the original dry sample. Iron was determined by the thiocyanate colorimetric method as given by Scott (11), and the pH determinations were made colorimetrically or by use of a quinhydrone electrode.

The following soils were used: black peat, organic matter in an advanced stage of decomposition; brown peat, organic matter partially decomposed; Edmonton loam, a mineral soil, high in organic matter; and Superior clay, a soil low in organic matter.

#### EFFECT OF LEACHING SOILS WITH ACID ON THEIR PHOSPHATE-FIXING POWER

The effect of leaching black peat with HCl solutions of different normalities on the phosphate-fixing power was determined as follows: Ten grams of peat were placed in a bottle with 250 cc. of the leaching solution and shaken for 30 minutes. The suspension was filtered, and the peat on the filter was leached first with an additional 250 cc. of the acid solution and then with water till free of chlorides. The fixing power of the leached material after being dried and pulverized was determined as previously outlined, and the results are given in table 1. These data show that leaching caused a depression in the phosphate-fixing power, the extent depending on the normality of the acid used. The original material fixed 45 to 72 per cent of the amount applied, but leaching with 0.05 *N* HCl reduced this to about 30 per cent. The material leached with 0.1 *N* acid fixed only 11 to 22 per cent of the applied phosphate, and that leached with *N* acid lost practically all fixing power. Normal HCl exerted considerable solvent action on the mineral fraction but not on the organic matter, indicating that the loss of fixing power was connected with the mineral material.

Further evidence regarding this loss of fixing power was obtained by determining the fixing power of the substances in the *N* HCl leachate. Aliquots of the leachate were measured out, the desired amount of phosphate was added, the solutions were evaporated, and the residues were extracted with the standard extracting solution. In a second set of aliquots, the iron and aluminum were precipitated with  $\text{NH}_4\text{OH}$  and separated by filtration. These hydroxides were then dissolved in dilute HCl, and the fixing power of the solutions was determined as with the original leachates. The data from these experiments, reported in table 2, show that the substances dissolved by the *N* HCl have fixed approximately all of the added phosphate, indicating even greater fixing power than the unleached peat (table 1). The data also show that the iron or the aluminum, or both, must be the active material in the fixation, for when separated from the extract and tested, it caused the fixation of as much phosphate as the original extract. The standard extracting solution undoubtedly had considerable solvent effect on any aluminum phosphate that was formed (12), but only slight solvent effect on the iron phosphate,

whose point of minimum solubility is approximately pH 3 (6). These results are in keeping with previous work on the fixation of phosphate by peat (3).

Since ferric iron does not ordinarily function as an exchangeable base, the fixation was probably not caused by exchangeable iron. Additional evidence that the fixing material did not exist in exchangeable form was obtained by leaching some peat with *N* KCl in the same manner as with HCl. The results,

TABLE 1  
*Phosphorus fixed by black peat before and after leaching with HCl and KCl*

P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT OF SAMPLE	P.P.M. PHOSPHORUS FIXED BY PEAT, BASED ON WEIGHT OF ORIGINAL SAMPLE				
	Unleached	Leached with 0.05 <i>N</i> HCl	Leached with 0.1 <i>N</i> HCl	Leached with <i>N</i> HCl	Leached with <i>N</i> KCl
50	36	17	11	6	29
100	67	30	22	-2	58
200	112	68	42	-4	104
500	227	160	54	14	234

TABLE 2  
*Phosphorus fixed by the substances in the *N* HCl extract of black peat*

P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT OF SOIL EXTRACTED	P.P.M. PHOSPHORUS FIXED, BASED ON WEIGHT OF SOIL EXTRACTED	
	By residue of HCl extract	By Fe and Al in HCl extract
50	50	48
100	92	97
200	190	192
400	387	382

TABLE 3  
*Phosphorus fixed by different soils before and after leaching with *N* HCl*

P.P.M. PHOS- PHORUS ADDED, BASED ON WEIGHT OF SAMPLE	P.P.M. PHOSPHORUS FIXED, BASED ON WEIGHT OF ORIGINAL SAMPLE					
	By brown peat		By Edmonton loam		By superior clay	
	Before leaching	After leaching	Before leaching	After leaching	Before leaching	After leaching
50	33	0	34	14	28	16
100	81	0	55	32	62	31
200	130	0	83	46	106	41

reported in table 1, and show that saturation of the exchange complex with potassium did not decrease the fixing power.

In order to determine whether the results obtained with black peat might apply generally, brown peat, Edmonton loam, and Superior clay were tested for fixing power before and after being leached with *N* HCl. Brown peat, like the black, lost its fixing power, and Edmonton loam and Superior clay lost about 50 per cent. The results are reported in table 3.

The leachate from the HCl extraction of the Superior clay was used for a subsequent series of experiments. In one series the fixing power of the residue of the leachate was determined as with the leachate from the peat. In a second series, the iron and aluminum in the leachate were separated from the other cations by precipitation with  $\text{NH}_4\text{OH}$ . The fixing power of the precipitated iron and aluminum hydroxides and of the residue of the leachate after removal of the iron and aluminum was tested in the regular way. Results are reported in table 4. These data show that the fixation by the residue of the leachate is due almost entirely to the iron and aluminum compounds present. The fixing power of the original soil was less than that of the HCl extract, although this soil did not lose all of its fixing power when leached (table 3). Apparently the fixing material became more reactive after solution and re-

TABLE 4  
*Phosphorus fixed by the substances in the N HCl extract of superior clay*

P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT OF SOIL EXTRACTED	P.P.M. PHOSPHORUS FIXED, BASED ON WEIGHT OF SOIL EXTRACTED		
	By residue of HCl extract	By Fe and Al ppt. from HCl extract	By residue of HCl extract after removal of Fe and Al
50	50	47	..
100	94	94	5
200	190	188	13
400	386	378	1

TABLE 5  
*Phosphorus fixed by black peat after leaching with NaOH and  $\text{NH}_4\text{OH}$*

P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT OF SAMPLE	P.P.M. PHOSPHORUS FIXED BY PEAT, BASED ON WEIGHT OF ORIGINAL SAMPLE		
	Unleached	Leached with 0.05 N NaOH	Leached with 0.5 N $\text{NH}_4\text{OH}$
50	36	47	43
100	67	88	81
200	112	148	132
500	227	395	...

precipitation. Iron may also have been brought into solution by the HCl from rather unreactive minerals. It is to be noted that Ford (5) attributes the fixation of phosphate in difficultly available form largely to the action of hydrated iron oxide, forming basic iron phosphate.

#### EFFECT OF LEACHING BLACK PEAT WITH A BASE ON ITS FIXING POWER

A sample of black peat was leached with 0.05 N NaOH, washed with water until the filtrate gave no color with phenolphthalein, and then dried. A second sample was similarly leached with 0.5 N  $\text{NH}_4\text{OH}$  and washed. The fixing power of the peat after these leachings is given in table 5; a comparison with the unleached samples shows that the fixing power has been increased. Leaching a soil with an alkaline solution tends to hydrolyze any iron phosphate

present, the iron remaining as the hydroxide and the phosphate leaching out. This increases the amount of free iron oxide in the soil and accounts for the increased fixing power.

These results are in accord with those of Russell and Prescott (10) who report that the removal of the humus material from a soil by leaching with NaOH did not destroy the power of the soil to fix phosphate. There is some evidence that the alkaline leachate of a soil contains phosphorus and iron in organic combination, for they are retained by the colloidal precipitate repeatedly formed by alternate precipitation with acid and solution with alkali.

#### FIXATION OF PHOSPHATE BY NATURAL AND SYNTHETIC HUMUS

Purified natural humus was prepared as follows: Forty grams of peat was shaken with 1 liter of 2 N NaOH for 30 minutes, and part of the liquid was decanted after settling. The suspension was repeatedly made up to 1 liter with water, shaken, and decanted after settling, until approximately 2 liters of

TABLE 6

*Phosphorus fixed by purified humus material extracted from peat by leaching with NaOH*

PHOSPHORUS AND COAGULANTS ADDED TO NaOH HUMUS SOLUTION	PHOSPHORUS		
	In solution	Extracted from precipitate by 0.002 N H <sub>2</sub> SO <sub>4</sub>	Total soluble
	mgm.	mgm.	mgm.
Check, coagulated with HCl.....	0.039	None	0.039
0.01 mgm. P added, coagulated with HCl.....	0.050	None	0.050
Check, coagulated with CaCl <sub>2</sub> .....	0.022	0.011	0.033
0.01 mgm. P added, coagulated with CaCl <sub>2</sub> .....	0.023	0.020	0.043

solution were obtained. This solution was filtered through paper pulp, and the humus purified by three alternate precipitations with HCl and re-solutions in alkali, after which it was dried and pulverized. A weighed amount of the humus was dissolved in a solution of NaOH. To aliquots of the humus solution, a known amount of phosphate and then HCl or CaCl<sub>2</sub> were added until the organic matter was coagulated. After filtering, the precipitates were washed with water, dried, and then extracted with the standard extracting solution. The phosphorus contents of these extracts and of the filtrates obtained after coagulation were determined, and the results are reported in table 6. These data show that coagulation of the organic matter with HCl did not cause a precipitation of phosphate, for all the added phosphate remained in solution. Coagulating the humus with CaCl<sub>2</sub> caused a precipitation of some of the added phosphate, as shown by the increase in phosphorus extracted from the precipitate. It was precipitated, apparently, as calcium phosphate. In neither case was there any fixation in difficultly available form.

Synthetic humus was prepared as outlined by Burke, Linweaver, and

Horner (2). Fifty-gram samples of dextrose were boiled in 250 cc. of 35 per cent HCl for 15 minutes over a low flame. Fifty milligrams of iron as ferric sulfate was added to one sample of dextrose before boiling. The solutions were filtered and the precipitates dissolved with KOH and reprecipitated with HCl four times. The precipitates were dried at 105°C. and pulverized. The purified precipitates contained the following amounts of phosphorus and iron:

	<i>Phosphorus per cent</i>	<i>Iron (Fe) per cent</i>
Check—iron not added. . . . .	0.0103	0.152
Iron added. . . . .	0.0131	0.218

The dextrose used contained phosphorus and iron as shown by the check sample. The addition of iron to the solution before beating caused a marked increase in the amount of phosphorus and iron found in the precipitate.

One-half gram samples of the synthetic humus were dissolved in KOH and diluted to 200 cc. Aliquots of these solutions were measured into evaporating dishes, and 0.01 mgm. of phosphorus was added. Hydrochloric acid was added to each until coagulation of the organic material took place, which was approximately at the neutral point. After evaporation on the steam bath, the residues were extracted with 50 cc. of standard extracting solution. The added phosphate was all recovered in both series. These results are similar to those obtained with natural humus.

Experiments using finely ground alfalfa and organic base exchange material as prepared by Mitchell (8) showed that these organic substances did not possess the power to fix phosphates.

Dumont (4) found that humus soil containing varying amounts of lime fixed more monocalcium phosphate than did mineral soils. This, however, is not fixation in difficultly available form. Bottini (1) advanced the theory of the formation of humo-phosphates, which are mixtures of calcium humate and calcium phosphate. These humo-phosphates are supposed to be formed only under neutral or alkaline conditions. Evidence of the formation of similar compounds was obtained in the present investigation when natural humus material was treated with phosphate and calcium chloride.

#### EFFECT OF OXIDATION WITH HYDROGEN PEROXIDE ON THE FIXING POWER OF BLACK PEAT

Hydrogen peroxide (approximately 30 per cent) was freed of phosphate by distilling under vacuum and collecting the distillate in a flask packed in ice. The strength is usually reduced somewhat by this distillation.

The black peat was oxidized by adding a small quantity of the purified hydrogen peroxide to the wet sample and heating on the steam bath until bubbling had practically ceased. This treatment was repeated until the desired degree of oxidation was obtained. The resulting suspension was then boiled for a few minutes, filtered, and the residue washed with hot water until it became practically free of soluble organic matter. The residue was dried, weighed, and then pulverized.

The fixing power of fractions of the residue equivalent to 1 gm. of the original peat was determined in the usual manner. Aliquots of the water filtrates and washings were also used for fixation tests. The results of these experiments are reported in table 7. These data show that the treatment with hydrogen peroxide has reduced the fixation of added phosphate from 157 p.p.m. in the untreated sample to 5 p.p.m. in the sample treated with 4 cc. of hydrogen peroxide per gram of soil. This reduction in fixing power is attributed to a partial saturation of the fixing material with the phosphate liberated from the organic matter during oxidation. The acidity developed in the solutions during oxidation was approximately pH 4, which would still permit the formation of ferric phosphate.

The substances in the water extracts and washings showed some fixing power, but not enough to account for the loss in the corresponding residues. There was a gradual increase in the amount of phosphorus fixed by the substances in the water extracts with increased oxidation. The increased oxida-

TABLE 7

*Phosphorus fixed by the residue and by the substances in the water extract of black peat after oxidation with hydrogen peroxide*

H <sub>2</sub> O <sub>2</sub> ADDED PER GM. PEAT	P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT OF ORIGINAL SAMPLE	P.P.M. PHOSPHORUS FIXED, BASED ON WEIGHT OF SAMPLE TREATED	
		By residue of water extract	By substances in water extract
cc.			
0	200	157	..
1	200	58	33
2	200	29	46
3	200	11	45
4	200	5	68

tion probably raised the amount of free ferric iron in the extracts, which would account for the greater fixation.

The oxidation of the peat brought large amounts of phosphorus and iron into solution. It was found that the water-soluble phosphorus increased from 15 p.p.m. when the soil was untreated to 334 p.p.m. when 4 cc. of hydrogen peroxide was used. Further oxidation, using as high as 30 cc. per gram of soil, caused only a slight additional increase. The water-soluble iron increased from 96 p.p.m. in the untreated to 4,960 p.p.m. when the peat was treated with 4 cc. of hydrogen peroxide per gram. At greater oxidation there was a still further increase.

These results are more or less in keeping with the work of Peterson (9), who found that approximately a maximum amount of phosphorus was made soluble in 0.2 *N* HNO<sub>3</sub> by the time one-third of the organic matter had been oxidized. He also found that the increase in soluble iron was roughly parallel, though not proportional, to the increase in soluble phosphorus.

The large amounts of iron in the water extracts following the hydrogen peroxide treatments should fix much more phosphate than is shown in table 7. Attempts to throw this iron out of solution with  $\text{NH}_4\text{OH}$  were unsuccessful, indicating that it must be held in combination with or protected by the organic matter, for if present in an inorganic form, it would have been precipitated.

The organic matter in a highly colored water extract of a peroxide-treated peat was destroyed by taking to dryness in the presence of hydrogen peroxide and then adding  $\text{H}_2\text{SO}_4$  and igniting. The residue was taken up in  $\text{HCl}$ , the iron precipitated with  $\text{NH}_4\text{OH}$ , and the precipitate washed and then dissolved in  $\text{HCl}$ . Aliquots of this solution were used for an iron determination and for fixation experiments. When phosphorus was added at the rate of 200 p.p.m., 190 p.p.m. were fixed. Since the extract contained approximately 3,000 p.p.m. of iron, the maximum fixing power possible was probably much higher than that indicated. The fixation was much greater than when the iron was combined with the organic matter (table 7).

Five peats were subjected to five successive oxidations with hydrogen peroxide to determine whether there exists a definite iron-phosphorus ratio in the material dissolved. The samples were washed free of soluble organic matter after each peroxide treatment. No definite iron-phosphorus ratio was found in the water-soluble material.

Samples of Goethite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), peat ash, and aliquots of an acid extract of peat were treated with hydrogen peroxide to determine the effect on their fixing power. In no case was there any apparent reduction in the fixing power.

#### EFFECT OF HEAT ON THE FIXING POWER OF BLACK PEAT AND GOETHITE

Samples of black peat and Goethite were heated for 2 hours at temperatures of 200°, 400°, 600°, and 800°C. in an electric furnace, and their fixing power was determined thereafter. Heating for 2 hours at 400°C. destroyed all organic matter. Because of the alkalinity of the peat ash, varying amounts of acid had to be added to the extracting solution to maintain the desired acidity, pH 3. The residues of the peat samples which had been heated at 800°C. were not so alkaline as those heated at 600°C., requiring only one-half as much acid to maintain a pH of 3. Reaction and combination of the bases with silica at the higher temperatures may have caused this.

The data in table 8 show that heating the peat at 200°C. for 2 hours caused a depression in its fixing power and an increase in soluble phosphorus. Ford (5) found that heating certain mineral soils at 210°C. for 13 days decreased their fixing power. He attributed the decrease to a dehydration of the Goethite which they supposedly contained. In table 8 it is found that heating Goethite for only 2 hours at 200°C. did not appreciably decrease its fixing power, but at higher temperatures there was a decided decrease. The residue of the peat heated at 400°C. had a slightly greater fixing power than the unheated peat. A further increase resulted at 600°C. The residues of the samples heated at



800°C. would not fix phosphate, probably because of the inactivation of the iron oxide.

The amount of soluble phosphorus in the peat residue increased from 12 to 304 p.p.m. when the temperature of heating was raised from 600° to 800°C. (table 8). This increase was probably caused by a breaking down of the ferric phosphates and the formation of ferric oxide and calcium phosphate. Similar results were obtained when mixtures of ferric phosphate and CaO were heated to 800°C.

Mitchell (8) found that heating a soil at 350°C. destroyed the organic base exchange complex. Since heating black peat at 400°C. for 2 hours did not reduce the fixing power (table 8), it appears that the organic base exchange complex does not enter into phosphate fixation.

TABLE 8

*Phosphorus soluble and fixed by black peat and Goethite before and after heating for 2 hours at various temperatures*

P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT ORIGINAL SAMPLE	P.P.M. PHOSPHORUS SOLUBLE IN 0.002 N H <sub>2</sub> SO <sub>4</sub> AND FIXED AFTER TREATMENTS INDICATED, BASED ON WEIGHT OF ORIGINAL SAMPLE									
	Check, unheated		Heated at 200°C.		Heated at 400°C.		Heated at 600°C.		Heated at 800°C.	
	Soluble	Fixed	Soluble	Fixed	Soluble	Fixed	Soluble	Fixed	Soluble	Fixed
<i>Peat</i>										
None	21	...	86	...	26	...	12	...	304	..
50	35	36	112	24	33	43	19	41	352	2
100	54	67	134	52	66	60	22	90	376	28
200	109	112	176	110	72	154	30	180	494	10
<i>Goethite</i>										
None	None	...	None	...	9	...	26	...	84	..
100	2	98	3	97	31	78	59	67	184	None

Kelley, Dore, and Brown (7) found that the exchange capacity of the inorganic soil colloids was reduced approximately two-thirds by heating at 600°C. Heating black peat at 600°C. did not cause any loss in power to fix phosphate, showing that the fixing power was not dependent on the exchange capacity of the inorganic base exchange complex.

#### EFFECT OF HEAT ON THE SOLUBILITY OF PHOSPHATIC COMPOUNDS OF IRON AND ALUMINUM IN 0.002 N H<sub>2</sub>SO<sub>4</sub>

The large increase in soluble phosphorus in the residues of the peat samples heated at 800°C. indicated that the ferric phosphates were being broken down and calcium phosphate was being formed. Additional evidence on this point was obtained as follows: One-tenth-gram samples of ordinary C.P. precipitated

iron and aluminum phosphates were heated in an electric furnace at various temperatures and then extracted with 100 cc. of the standard extracting solution. To a set of duplicate samples, 0.06 gm. of CaO was added before heating. The samples were placed in the cold furnace and removed when the desired temperature was reached. Sufficient  $H_2SO_4$  was added to the extracting solution to neutralize the CaO and maintain the solution at pH 3. The samples were heated in Sillimanite crucibles to prevent a reaction between the crucible and sample at the higher temperatures.

The data in table 9 show that heating the ferric phosphate alone at 800°C. decreased the soluble phosphorus from 0.138 mgm. to 0.072 mgm. The decrease is attributed to a dehydration of the ferric phosphate at the higher temperatures, though part of the effect may be due to a slight change in physical condition, thus reducing the surface exposed. The increased solubility of phosphorus when the ferric phosphate was heated with CaO is probably

TABLE 9

*Phosphorus dissolved from 0.1-gm. samples of  $FePO_4$  and  $AlPO_4$  by 0.002 N  $H_2SO_4$ , before and after being heated alone and with CaO*

TEMPERATURE OF HEATING	PHOSPHORUS DISSOLVED BY 0.002 N $H_2SO_4$ BEFORE AND AFTER HEATING OF MATERIALS INDICATED			
	$FePO_4$	$FePO_4 + CaO$	$AlPO_4$	$AlPO_4 + CaO$
°C.	mgm.	mgm.	mgm.	mgm.
Unheated	0.138	0.131	0.90	1.09
200	0.148	0.143	1.36	1.79
400	0.152	0.164	.....	.....
500	.....	.....	0.86	1.49
600	0.116	0.915	0.03	0.195
700	0.092	1.78	.....	.....
800	0.072	2.58	0.012	0.545

caused by a breaking down of the ferric phosphate and the formation of ferric oxide and calcium phosphate. This reaction began at approximately 600°C., although a greater recovery of phosphate was obtained by heating to 800°C.

Four samples of natural hydrated iron oxides containing some phosphorus, probably as basic ferric phosphate, showed a large increase in phosphorus soluble in 0.002 N  $H_2SO_4$  when heated to 800°C.

When the  $AlPO_4$  was heated to 200°C. the soluble phosphorus increased; when it was heated to 500°C., the soluble phosphorus was about the same in amount as for the unheated material; but at 600° and 800°C., the soluble phosphorus was greatly decreased. At 500°C. the  $AlPO_4$  showed a slight tendency to fuse, and at 600°C. and over, it fused into hard lumps. The decreased solubility may have been due to the decreased surface, although pulverizing in an agate mortar did not increase the solubility to that of the original material. If the same degree of fineness as that of the original material had been obtained, the solubility might have been the same as the original. When

CaO was mixed with the  $\text{AlPO}_4$  there was a very decided decrease in soluble phosphorus after heating to  $600^\circ\text{C}$ . The solubility after heating to  $800^\circ\text{C}$ . was approximately one-half that of the unheated material, though greater than when heated to  $600^\circ\text{C}$ . The amount of fusion was not so great in the presence of the CaO, although there was a tendency to form hard particles at  $600^\circ$  and  $800^\circ\text{C}$ . Peterson (9) found that heating wavellite at  $185^\circ$  and  $240^\circ\text{C}$ . increased the amount of phosphorus soluble in  $0.2\text{ N HNO}_3$ .

A sample of apatite gave no increase in soluble phosphorus when heated to  $800^\circ\text{C}$ . When the apatite was mixed with CaO and then heated to  $800^\circ\text{C}$ . the amount of soluble phosphorus was reduced approximately 50 per cent.

From the foregoing results it is evident that the increase in soluble phosphorus when the peat was heated at  $800^\circ\text{C}$ . (table 8) was caused by a breaking down of the ferric phosphates, because of reaction with lime and other bases.

#### SUMMARY

Experiments were conducted to determine the effect of the following treatments on the power of the organic matter of soils to fix added phosphate: (a) leaching with HCl; (b) leaching with NaOH and  $\text{NH}_4\text{OH}$ ; (c) oxidation of the organic matter with hydrogen peroxide; (d) heating at temperatures up to  $800^\circ\text{C}$ . The fixation of phosphate by natural and synthetic humus material and the effect of heat on the solubility of two phosphatic compounds were also studied.

Leaching the soils with HCl reduced the fixing power for added phosphates. The ferric iron in the acid leachings possessed somewhat greater fixing power than the soils from which these leachings were derived.

Leaching peat with NaOH or  $\text{NH}_4\text{OH}$  increased its fixing power because of an increase in active iron. The alkaline extracts did not fix phosphates.

Natural and synthetic humus did not fix phosphate.

Oxidation of the organic material with hydrogen peroxide decreased the power of soils to fix added phosphates, the decrease being greater where the oxidation was greater. This loss of fixing power is attributed to a saturation of the fixing material with phosphorus liberated from organic compounds during oxidation.

Heating peat at  $600^\circ\text{C}$ . for 2 hours did not destroy its power to fix phosphate. Heating at  $800^\circ\text{C}$ . for 2 hours caused a complete loss of fixing power. The increase in phosphorus soluble in  $0.002\text{ N H}_2\text{SO}_4$  when peat was heated at  $800^\circ\text{C}$  is attributed to reaction of ferric phosphates with lime to form calcium phosphate.

Heating a mixture of ferric phosphate and CaO to  $800^\circ\text{C}$ . caused a large increase in phosphorus soluble in  $0.002\text{ N H}_2\text{SO}_4$ . When  $\text{AlPO}_4$  was heated under the same conditions there was less soluble phosphorus than in the unheated material.

The evidence shows that soil organic matter as such has only a minor rôle, if any, in the fixation of phosphorus in difficultly available form when soluble phosphatic fertilizers are applied to a soil.

## REFERENCES

- (1) BOTTINI, E. 1925 Humophosphates. *Ann. Chim. Appl.* 15: 358-362; *Chem. Abst* 20: 257.
- (2) BURK, D., LINWEAVER, H., AND HORNER, C. K. 1932 Iron in relation to the stimulation of growth by humic acid. *Soil Sci.* 33: 413-453.
- (3) DOUGHTY, J. L. 1929 The fixation of phosphate by a peat soil. *Soil Sci.* 29: 23-35.
- (4) DUMONT, J. 1901 On the adsorption of monocalcium phosphate by arable soil and by humus. *Compt. Rend. Acad. Sci. [Paris]* 132: 435-437.
- (5) FORD, M. C. 1933 The nature of phosphate fixation in soils. *Jour. Amer. Soc. Agron.* 25: 134-144.
- (6) GAARDER, T. 1930 Die Bindung der Phosphorsaure im Erdboden. Vestlandets Forstl. Forsøkssta. Meddel. 14.
- (7) KELLEY, W. P., DORE, W. H., AND BROWN, S. H. 1931 The nature of the base exchange material of bentonite, soils, and zeolites, as revealed by chemical investigation and X-ray analysis. *Soil Sci.* 31: 25-55.
- (8) MITCHELL, J. 1932 The origin, nature and importance of soil organic constituents having base exchange properties. *Jour. Amer. Soc. Agron.* 24: 256-275.
- (9) PETERSON, P. P. 1911 Effect of heat and oxidation on the phosphorus of the soil. *Wis. Agr. Exp. Sta. Res. Bul.* 19.
- (10) RUSSELL, E. J., AND PRESCOTT, J. A. 1916-17 The reaction between dilute acids and the phosphorus compounds of the soil. *Jour. Agr. Sci.* 8: 65-110.
- (11) SCOTT, W. W. 1917 Standard Methods of Chemical Analysis, ed. 2. Van Nostrand Co., New York.
- (12) TEAKLE, L. J. H. 1928 Phosphate in the soil solution as affected by reaction and cation concentrations. *Soil Sci.* 25: 143-162.
- (13) TRUOG, E. 1930 The determination of the readily available phosphorus of soils. *Jour. Amer. Soc. Agron.* 22: 874-882.
- (14) TRUOG, E., AND MEYER, A. H. 1929 Improvements in the Denigés colorimetric method for phosphorus and arsenic. *Indus. and Engin. Chem. Anal. Ed.* 1: 136-139.

# FLUORINE, ITS EFFECT ON PLANT GROWTH AND ITS RELATION TO THE AVAILABILITY TO PLANTS OF PHOSPHORUS IN PHOSPHATE ROCKS<sup>1</sup>

R. P. BARTHOLOMEW<sup>2</sup>

*Arkansas Agricultural Experiment Station*

Received for publication September 28, 1934

Fluorine occurs naturally in phosphate rocks (10) which are used in the manufacture of superphosphates and is also found in the manufactured product in amounts varying from about 1 to 3 per cent.<sup>3</sup> The addition of these compounds to the soil incorporates appreciable quantities of fluorine in the soil. The use of fluorides and fluosilicates as insecticides will also add fluorine to soils. Fluorine compounds have been reported to increase plant growth under certain conditions and to decrease it under others. Gautier and Clausman (9) report that the application of 100 p.p.m. of fluorine as calcium fluoride to field plots definitely increased the yield of some plots. Mazé (11) states that fluorine is indispensable for the growth of corn. Aso (1, 2) found differences in the effect of sodium fluoride and sodium silico-fluoride on the growth of plants in solution cultures. Some plants were able to develop normally in concentrations of 0.001 per cent, whereas others were killed at that concentration. Greater concentrations than 0.001 per cent of either salt were injurious to all plants used. Wilson (13) and Wöber (14) report that fluorine has a toxic effect on the development of certain plants. With such divergent results from the few experiments reported, more information on the effect of fluorine on plant growth is desirable.

Fluorine could affect the growth of plants in several ways. The results in this report are concerned with the effect of fluorine on the germination of seeds, the production of dry matter by plants, and the availability of phosphorus from various phosphates.

## EFFECT OF FLUORINE ON GERMINATION

Sudan grass, cowpea, soybean, red clover, and white Dutch clover seeds were germinated according to the official method of the State Seed Laboratory, modified so that solutions containing known amounts of fluorine as sodium or

<sup>1</sup> Published with the approval of the director. Research paper No. 388, Journal Series, University of Arkansas.

<sup>2</sup> Associate Agronomist.

<sup>3</sup> Hill, W. L. 1934 Private communication. Bur. Chem. and Soils, U. S. Dept Agr., Washington, D. C.

calcium fluoride were used instead of water in wetting the germination pads. The largest concentration of fluorine used is greater than would be added to soils in heavy applications of known phosphates. The results are given in table 1.

The results with Sudan grass are nearly all lower when fluoride solutions are used in wetting the germination pads. The differences, with the exception of 1 p.p.m. of fluorine as sodium fluoride and 3 p.p.m. as calcium fluoride are

TABLE 1  
*Effect of varying concentrations of fluorine compounds on the germination of seeds*

SOURCE OF FLUORINE	CONCENTRATION OF F	VIABLE SEED					
		Sudan grass A	Sudan grass B	Cowpea	Soybean	White Dutch clover	Red clover
	p.p.m.	per cent	per cent	per cent	per cent	per cent	per cent
None.....	0	83.5	89.5	79.0	91.5	31.0	66.0
NaF.....	0.25	77.0	....	79.0	93.5	29.5	64.5
NaF.....	0.50	79.0	....	77.5	86.5	31.5	63.0
NaF.....	1.00	72.0	....	79.5	91.5	32.5	58.0
NaF.....	3.00	81.0	....	80.0	92.0	32.0	59.5
NaF.....	5.00	77.0	....	78.0	91.5	32.0	59.5
NaF.....	10.00	....	85.5	....	90.0	39.0	61.5
NaF.....	50.00	....	89.5	....	84.0	35.5	61.5
CaF <sub>2</sub> .....	0.25	80.0	....	80.0	91.5	42.5	58.5
CaF <sub>2</sub> .....	0.50	81.5	....	83.5	92.5	45.5	58.5
CaF <sub>2</sub> .....	1.00	80.0	....	81.5	91.0	39.5	60.5
CaF <sub>2</sub> .....	3.00	71.5	....	80.0	90.0	42.0	65.0
CaF <sub>2</sub> .....	5.00	80.0	....	75.5	89.5	43.0	62.0
CaF <sub>2</sub> .....	7.72	....	....	....	89.5	52.5	56.5
Na <sub>2</sub> SiF <sub>6</sub> .....	0.25	....	88.0	....	89.5	39.0	68.0
Na <sub>2</sub> SiF <sub>6</sub> .....	0.50	....	88.5	....	91.5	47.5	54.0
Na <sub>2</sub> SiF <sub>6</sub> .....	1.00	....	87.5	....	91.5	50.0	60.0
Na <sub>2</sub> SiF <sub>6</sub> .....	3.00	....	89.5	....	88.5	48.0	55.5
Na <sub>2</sub> SiF <sub>6</sub> .....	5.00	....	91.0	....	91.0	49.0	63.5
Na <sub>2</sub> SiF <sub>6</sub> .....	10.00	....	88.5	....	94.0	45.5	58.0
Na <sub>2</sub> SiF <sub>6</sub> .....	50.00	....	87.0	....	91.5	50.0	59.5

within the limits of error allowed in germination tests. The results from the cowpeas and soybeans show no injurious effect on the germination of these seeds. Although the red clover and white Dutch clover were old seeds the results give little evidence of decreased germinations because of the fluorine added. The results with red clover excepting the 0.5 and 3.0 p.p.m. of fluorine as sodium fluosilicate are within the limits of error allowed. The use of fluorine as calcium fluoride and sodium fluosilicate increased the percentage of germination from white Dutch clover. The results all show

that fluorine as sodium or calcium fluoride and sodium fluosilicate had little, if any, injurious effect on the germination of the seeds used.

#### EFFECT OF FLUORINE ON THE PRODUCTION OF DRY MATTER

Several experiments using cowpeas as the test crop were conducted in solution cultures similar to those previously reported (4). The seedlings were transferred from sand to the culture solution when the first leaves were formed and were permitted to grow for 10 days before the fluorine treatments were given. One plant was grown per jar in the first series, four in the second series, and three in the last series. In 1932 the fluorine compounds were added directly to the culture solutions, whereas in the other series separate jars were used for the fluorine compounds and the plants were permitted to grow for alternate periods in each solution. In the second series the fluorine solutions were renewed weekly, and after it was found that, because of absorption of fluorine in varying amounts by the plants, the initial concentrations of fluorine were not being maintained, the crop was harvested and the third series started. In this series the fluorine solutions were renewed daily. Iron was given as needed by placing the plants for several hours in an iron citrate solution having a pH of 4. Sodium fluoride was used as the standard fluorine treatment, and calcium fluoride and sodium fluosilicate were used as supplementary treatments. The concentrations of fluorine used were selected as being comparable to those which might develop in the soil solution after fluorine-bearing compounds were added to the soil. The plants in the first series were permitted to grow almost twice as long as the third series.

There were slight reductions in the amount of dry matter produced where fluorine was added in the 1932 series but in most cases they were less than 12 per cent, usually about 5 per cent, and could be attributed to plant variation or experimental error (table 2).

It should be mentioned that in the second series not only were the plants in different jars depleting the concentration of fluorine at different rates, as determined by analyses of the culture solutions, but great differences in appearance existed in the plants on duplicate jars. Prior to the time of harvesting, small areas in the center of the leaves had died and in some cases the dead areas spread to include the whole leaf. Microscopical examination revealed bacteria in cross-sections of the stems but not in any of the leaf areas. Although the dead spots in the leaves may have been due to the bacterial infection and not to the presence of fluorine, the appearance did not indicate that such was the case. However, there was no way of determining whether the injury was caused by the presence of fluorine.

In the third series where the concentrations of fluorine were maintained as nearly constant as possible, the results are decidedly variable. In general the results agree with those from the other two series in showing very little decrease in dry weight which can be attributed to the presence of fluorine. For example the dry weight of the plants where 3 p.p.m. of fluorine was added

as sodium fluoride was only 8.5 gm. as compared to 18.5 gm. for the check and 18.6 gm. where 5 p.p.m. of fluorine was added. This decrease was undoubtedly caused by plant variation.

The results from the three series as a whole indicate that soluble fluorine in concentrations under 10 p.p.m. had decreased very little, if any, the amounts of dry matter produced by cowpeas growing in solution cultures.

#### FLUORINE AND PHOSPHORUS CONTENT OF PLANTS

The roots and tops were ground and analyzed separately for fluorine and phosphorus. The fluorine was distilled from the plant tissue after the method of Willard and Winter (12) and either titrated according to that method or

TABLE 2

*Dry weight of cowpeas grown in nutrient solution with the concentration of fluorine indicated*

SOURCE OF FLUORINE	CONCENTRATION OF FLUORINE	1932	1933-A	1933-B	
		Average dry weight one plant	Average dry weight four plants	Average dry weight three plants	
				Tops	Roots
	p.p.m.	gm.	gm.	gm.	gm.
None.....	0	17.7	8.3	18.5	9.2
NaF.....	0.25	15.5	6.6	21.2	9.5
NaF.....	0.50	16.7	9.4	21.6	10.9
NaF.....	1.00	13.9	7.3	33.2	16.7
NaF.....	3.00	13.0	8.8	8.5	5.5
NaF.....	5.00	17.9	9.9	18.6	9.8
NaF.....	10.00	15.4	10.2	10.9	6.8
CaF <sub>2</sub> .....	0.25	18.5	8.4	13.3	9.3
CaF <sub>2</sub> .....	0.50	15.8	7.0	24.9	11.8
CaF <sub>2</sub> .....	7.72	16.7	5.5	17.2	9.4
Na <sub>2</sub> SiF <sub>6</sub> .....	0.25	15.1	15.3	21.3	12.6
Na <sub>2</sub> SiF <sub>6</sub> .....	0.50	13.2	7.3	19.2	11.1
Na <sub>2</sub> SiF <sub>6</sub> .....	1.00	16.6	7.0	12.5	7.6
Na <sub>2</sub> SiF <sub>6</sub> .....	10.00	16.3	1.9	15.6	7.5

determined colorimetrically by the Foster method (7). Phosphorus was determined volumetrically in a nitric acid extract of the residue from a magnesium nitrate fusion. The result of duplicate analyses on duplicate treatments are given in table 3.

The results show that fluorine may be absorbed in appreciable quantities by plants, particularly when the concentration of fluorine in solution is relatively high. It is of especial importance to note that most of the fluorine was found in the roots of the plants and that with one exception the roots also contained a higher percentage of phosphorus than the tops of the Sudan grass. This is in agreement with the results reported by Gautier and Clausman (8). On the contrary, however, as the fluorine content of the tops increases,

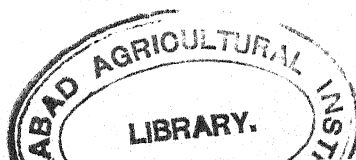


TABLE 3

*Phosphorus and fluorine content of cowpeas grown in complete nutrient solution and fluorine-containing solutions as indicated*

SOURCE OF FLUORINE	CONCENTRATION OF FLUORINE	ROOTS		TOPS	
		P	F	P	F
	<i>p.p.m.</i>	<i>per cent</i>	<i>p.p.m.</i>	<i>per cent</i>	<i>p.p.m.</i>
None.....	0	0.200 0.218	0.0 0.0	0.148 0.153	0.0 0.0
NaF.....	0.25	0.213 0.185	13.7 58.0	0.135 0.167	0.0 0.0
NaF.....	0.50	0.240 0.223	13.7 8.0	0.153 0.125	0.0 0.0
NaF.....	1.00	0.223 0.220	60.0 39.1	0.102 0.125	0.0 0.0
NaF.....	3.00	0.248 0.298	237.5 550.0	0.125 0.180	0.0 8.0
NaF.....	5.00	0.195 0.215	838.0 427.0	0.110 0.113	63.7 63.7
NaF.....	10.00	0.200 0.200	826.0 1,086.0	0.135 0.118	26.2 40.0
CaF <sub>2</sub> .....	0.25	0.228 0.238	0.0 0.0	0.155 0.148	0.0 0.0
CaF <sub>2</sub> .....	0.50	0.170 0.180	0.0 0.0	0.130 0.145	0.0 0.0
CaF <sub>2</sub> .....	7.72	0.215 0.182	84.3 78.3	0.248 0.128	0.0 11.0
Na <sub>2</sub> SiF <sub>6</sub> .....	0.25	0.203 0.155	0.0 0.0	0.135 *	0.0 *
Na <sub>2</sub> SiF <sub>6</sub> .....	0.50	0.185 0.200	0.0 13.7	0.140 0.130	0.0 0.0
Na <sub>2</sub> SiF <sub>6</sub> .....	1.00	0.203 0.190	37.4 42.7	0.128 0.128	0.0 0.0
Na <sub>2</sub> SiF <sub>6</sub> .....	10.00	0.193 0.195	1,970.0 1,116.0	0.108 0.105	415.0 475.0

\* Sample lost.



there is a tendency for the percentage of phosphorus to decrease. A general trend for the percentage of phosphorus in the tops to decrease as the percentage of fluorine in the roots increases is also shown. Furthermore, fluorine was found in the tops of only those plants containing large amounts of fluorine in the roots. There is, however, no specific correlation between the percentage of fluorine in the plant and the percentage of phosphorus in the plant.

When it is observed that fluorine was present in many of the roots of the plant and in only a few instances in the tops, the question may well be raised as to what prevents the fluorine from moving into the tops of the plants.

There are two possible explanations for this situation, both of which are based on the precipitation of the fluorine either inside the roots or on the surface of the roots. Experiments with solutions of  $K_2HPO_4$ ,  $CaH_4(PO_4)_2 \cdot H_2O$ , and  $CaF_2$  gave results which showed that after the solutions had stood for one week no precipitate was formed in solutions containing 5 p.p.m. of P as  $K_2HPO_4$  and increasing amounts of F up to 7 p.p.m. as  $CaF_2$ . On the other hand, a slight cloudiness developed in a few hours when 5 p.p.m. F as  $CaF_2$  was added to a solution containing 5 p.p.m. of P as  $CaH_4(PO_4)_2 \cdot H_2O$ . No precipitate was formed when only 3 p.p.m. F was added as  $CaF_2$ . Although the precipitate was very slight, its presence was definitely established by means of a photo-electric cell. The reduction in light intensity was equivalent to 7 microamperes when the light was passed through the solution containing the precipitate. Because of the small amount and the colloidal nature of the precipitate, a sufficient amount for analysis could not be obtained. From a theoretical consideration the precipitate was presumably some form of a calcium fluophosphate. The solubilities as given by Comey (5) for  $Ca_3(PO_4)_2$  vary from 10 to 100 mgm. per liter; for  $CaF_2$ , from 14 to 16 mgm. per liter; and for fluorapatite, only 2 mgm. per liter. This assumption is substantiated in part by the results from the growth of Sudan grass in culture solutions containing fluorine. As previously stated, the greatest concentrations of fluorine and phosphorus were found in the roots and in many cases no fluorine was found in the tops, indicating that it had been precipitated from solution before it reached the tops of the plants.

A similar reaction to that described may be one of the factors preventing the efficient utilization of phosphorus in rock phosphate by crops.

#### AVAILABILITY OF FLUORINE-BEARING PHOSPHATES

Many studies have been made concerning the availability of rock phosphates to plants. The results of these studies have been conclusive in showing that rock phosphate was not an efficient source of phosphorus for the fertilization of many plants. Since fluorine is a constituent of most rock phosphates, experiments were started to determine whether its presence had any influence on the availability of rock phosphates for plant growth.

Cowpea plants were germinated in sand and placed in 2-liter percolators in culture solutions similar, except for phosphates, to those used in the foregoing

experiments. Equivalent amounts of phosphates, however, were placed in collodion bags, distilled water was added, and the bags were fastened so that phosphorus could get into the nutrient solution only by dialysis. The results from this experiment are given in table 4.

The results show that rock phosphate made poor growth as compared to monocalcium phosphate and precipitated tri-calcium phosphate. This will be discussed further.

Another series was conducted with cowpeas, four plants per jar, in jars containing 7.5 liters of culture solution. Phosphorus was added as monocalcium phosphate, precipitated tri-calcium phosphate, ammoniated superphosphate, rock phosphate, and fluorapatite to duplicate jars in amounts

TABLE 4  
*Green weight of cowpea plants grown with phosphate fertilization indicated*

SOURCE OF P	AVERAGE GREEN WEIGHT PER PLANT
	gm.
$\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ .....	19.25
$\text{Ca}_3(\text{PO}_4)_2$ .....	13.0
Rock phosphate (Ruhms) .....	4.5

TABLE 5  
*Dialyzed phosphorus in solution after 24- and 48-hour intervals*

SOURCE OF P	CONCENTRATION OF P IN SOLUTION	
	24 hours	48 hours
	p.p.m.	p.p.m.
$\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ .....	0.0125	0.0225
$\text{Ca}_3(\text{PO}_4)_2$ .....	0.5213	1.3900
Ammoniated superphosphate .....	0.3225	0.7710
Rock phosphate (Ruhms) .....	0.0125	0.01875
Fluorapatite .....	0.0100	0.01375

equivalent to 300 mgm.  $\text{P}_2\text{O}_5$  per jar. The phosphate for each jar was divided into equal parts and placed in two collodion bags, one of which was weighted with quartz pebbles to hold it on the bottom of the jar. After the bags had been sealed as in the preceding experiment, they were placed in the culture solution. The culture solutions were maintained as 7.5 liters by the daily addition of distilled water. The solutions were renewed at the end of 4 weeks, and a fresh addition of phosphorus was made in the same manner as described.

The discarded bags containing phosphorus were each placed in a liter of distilled water, and after 24 and 48 hours aliquots were analyzed by the Deniges blue color method (6) to determine the rate at which phosphorus was being dialyzed. The results are given in table 5.

The results indicate that all of the phosphorus from monocalcium phosphate had been dialyzed but that phosphorus was still coming into solution from the other compounds although in very small amounts from rock phosphate and fluorapatite. The results for ammoniated superphosphate do not permit a differentiation between it and precipitated tri-calcium phosphate, although it will be shown later that the smaller concentration in solution was in all probability due to a slower rate of dialysis and not due to previous utilization of the phosphorus.

TABLE 6

*Daily concentration of phosphorus in solution, dialyzed from the compounds indicated*

SOURCE OF P	CONCENTRATION OF P ON FOLLOWING DATES IN JUNE, 1933											
	3	4	5	6	7	8	10	11	12	15	16	
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	
CaH <sub>4</sub> (PO <sub>4</sub> )·H <sub>2</sub> O . . . . .	8.080	10.420	11.830	10.040	8.090	7.130	2.230	0.590	0.156	7.726*	6.250	
Ca <sub>3</sub> PO <sub>4</sub> . . . . .	0.031	0.169	0.045	0.049	0.044	0.021	†	0.018	0.021	0.017*	0.01	
Ammoniated superphosphate . . . . .	0.021	0.060	0.084	0.143	0.072	0.029	0.019	0.009	0.006	0.016*	0.015	
Rock phosphate (Ruhms) . . . . .	0.015	0.010	0.011	0.011	0.007	0.003	0.003	0.001	0.001	0.008*	0.002	
Fluorapatite . . . . .	0.012	0.006	0.014	0.014	0.011	0.002	0.004	0.002	0.002	0.002*	0.003	

\* Renewed phosphorus in new collodion bags.

† Beakers broke during analysis.

TABLE 7

*Dry weights of cowpea plants grown with the source of phosphorus indicated and supplied by dialysis from a collodion membrane*

SOURCE OF P	AVERAGE OVEN-DRY WEIGHT 4 plants	
	Tops	Roots
	gm.	gm.
$\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ . . . . .	28.7	7.1
$\text{Ca}_3(\text{PO}_4)_2$ . . . . .	17.1	7.3
Ammoniated superphosphate . . . . .	11.0	5.1
Rock phosphate (Ruhms) . . . . .	1.4	1.6
Fluorapatite . . . . .	1.6	1.9

Because of the large differences already noted, analyses were made on samples of solution taken at frequent intervals from the renewed culture solutions in which the plants were growing. The results are given in table 6.

The results show that monocalcium phosphate dialyzes very readily through the collodion membrane used, whereas the other compounds move through the membrane in much smaller amounts. It is presumed that this difference is the result of differences in the solubility of the compounds, although the rate of permeability of the compounds may differ. The amounts of phosphorus

found in the solutions containing rock phosphate and fluorapatite were very small. The large decreases in concentration of phosphorus in solution after the first few days were undoubtedly caused by the increased feeding as the plants and roots increased in size.

The amounts of dry matter produced by cowpeas in these experiments are given in table 7. The results show a wide variation in the ability of the phosphates to supply the plants with phosphorus when the phosphorus has to dialyze through a collodion membrane. A similar condition may exist in soils. The colloidal material in the soil separating the roots and the soil particle may act as a membrane through which the phosphorus must be dialyzed before the plants can absorb it. Similarly, particles of solid phosphates such as rock phosphate may be covered with a thin layer of colloidal matter which may act as a dialyzing membrane.

To study further the availability of rock phosphate another experiment was started in culture solutions in which equivalent amounts of phosphorus as monocalcium phosphate and rock phosphate in collodion bags were compared

TABLE 8  
*Dry weights of cowpea plants grown as described*

SOURCE OF P	AVERAGE DRY WEIGHT OF PLANTS	
	Tops	Roots
	gm.	gm.
$\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , in collodion bag.....	5.65	2.10
Rock Phosphate, in collodion bag.....	0.40	0.45
Rock Phosphate, saturated solution.....	4.90	1.85

with a saturated solution of rock phosphate. Cowpeas were again used as the test crops in the same nutrient solution as that used for the experiments already described. The saturated solution of rock phosphate was prepared by shaking 2 gm. of rock phosphate at frequent intervals for 5 days and then clarifying it by passing the solution through a Pasteur-Chamberlain filter. The concentration of phosphorus in the saturated solution of rock phosphate varied from 0.217 p.p.m. to 0.250 p.p.m., usually being closer to the latter figure. The solutions for the plants grown in the saturated solution of rock phosphate were changed twice daily in order to maintain the concentration of phosphorus as near its maximum as possible. The amounts of dry matter produced in 4 weeks from the different treatments are given in table 8.

The results show that when the phosphorus in solution from rock phosphate is maintained near its maximum concentration, the plants will make satisfactory growth. The plants in this case made almost as good growth as from the monocalcium phosphate. On the other hand, when the phosphorus had to dialyze from rock phosphate the growth was very unsatisfactory and amounted to only a small percentage of that made from monocalcium phosphate. Since

it has been shown previously (3) that cowpeas cannot utilize rock phosphate when applied in the solid form to quartz cultures, the evidence seems conclusive that the availability of rock phosphate is definitely associated with its rate of solution. The technique used did not permit testing the various theories which have been advanced governing the solubility of rock phosphate.

It was pointed out in the first experiments that the high phosphorus content of the roots may be associated with their fluorine content and that the presence of fluorine may be a factor in the availability of phosphorus to plants. Jacob<sup>4</sup>

TABLE 9  
*Analysis of fluorine-bearing materials*

MATERIAL	FLUORINE	P <sub>2</sub> O <sub>5</sub>	
		Total	Citrate-insoluble
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
(a) Calcium fluoride, synthetic.....	48.30	.....	.....
(b) Calcium fluoride, natural.....	46.20	.....	.....
(c) Sodium fluoride, 99.1 per cent NaF.....	44.80	.....	.....
(c) Sodium fluosilicate, 99.7 per cent Na <sub>2</sub> SiF <sub>6</sub> ...	60.40	.....	.....
(c) (d) Sodium aluminum fluoride, synthetic, 94.3 per cent Na <sub>3</sub> AlF <sub>6</sub> .....	51.20	.....	.....
(c) (d) Barium fluosilicate, 76.1 per cent BaSiF <sub>6</sub> , 2.8 per cent BaF <sub>2</sub> , remainder principally silica.....	31.60	.....	.....
(e) Fluorspar basic slag, No. B-11.....	1.29	11.06	9.21
(e) Curacao phosphate rock, No. 943.....	0.41	39.99	33.87
(e) Curacao phosphate rock, No. 985.....	0.70	38.22	33.80
(e) Christmas Island phosphate rock, No. 452...	1.32	39.27	34.80
(e) Nauru Island phosphate rock, No. 1160.....	2.10	38.66	33.97
(e) Ocean Island phosphate rock, No. 451.....	2.97	40.15	37.51
(e) Tennessee brown-rock phosphate, No. B-14..	3.79	33.86	31.19

(a) Made by double decomposition between calcium chloride and sodium fluoride.

(b) Fluorspar, Bureau of Standards sample 79.

(c) Sample supplied by the Insecticide Division, Bureau of Chemistry and Soils.

(d) Commercial insecticide material.

(e) Ground to 100 mesh.

has shown a definite relationship between the fluorine content of some phosphate rocks and the availability of the phosphorus as measured by chemical methods.

In order to test the effect of fluorine on the solubility of phosphorus in soils, varying amounts of fluorides and phosphates containing different percentages of fluorine were added to jars, each containing 10 kilos of Clarksville silt loam. The composition of the fluorine compounds<sup>5</sup> is given in table 9.

<sup>4</sup> Jacob, K. D. 1934 Private communication. Bur. Chem. and Soils, U. S. Dept. Agr., Washington, D. C.

<sup>5</sup> The writer is indebted to K. D. Jacob, Bureau of Chemistry and Soils, for the samples and analyses of the materials given in table 9.

The amounts of fluorine added were varied from 1 to 10 p.p.m. in order to simulate the fluorine content of the phosphates used. The phosphorus was

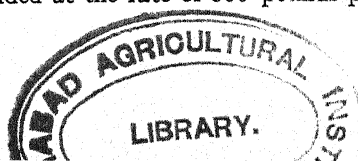
TABLE 10

*Yields of Sudan grass grown in Clarksville silt loam with the variation in fluorine and phosphorus treatment indicated*

SOURCE OF PHOSPHORUS	SOURCE OF FLUORINE	CONCENTRATION OF F IN THE SOIL	AVERAGE YIELD OVEN-DRY MATTER		
			First cutting	Second cutting	Total
		p.p.m.	gm.	gm.	gm.
None*	None	....	2.00	5.35	7.35
None	None	....	2.25	9.70	11.95
None	CaF <sub>2</sub>	1.0	2.35	8.85	11.20
None	CaF <sub>2</sub>	3.0	2.30	8.65	10.95
None	CaF <sub>2</sub>	5.0	1.75	8.10	9.85
None	CaF <sub>2</sub>	10.0	2.45	9.10	11.55
None	NaF	1.0	2.00	8.35	10.35
None	NaF	3.0	1.85	8.35	10.20
None	NaF	5.0	2.10	9.50	11.60
None	NaF	10.0	2.40	8.95	11.35
None	BaSiF <sub>6</sub>	1.5	1.90	7.30	9.20
None	BaSiF <sub>6</sub>	3.0	2.70	8.80	11.50
None	Na <sub>3</sub> AlF <sub>6</sub>	3.0	2.40	8.15	10.55
None	Na <sub>2</sub> SiF <sub>6</sub>	3.0	2.45	7.60	10.05
Fluorspar basic slag	Fluorspar basic slag	3.5	6.40	16.05	22.45
Phosphate rock 943	Phosphate rock	0.3	21.70	23.35	45.05
Phosphate rock 985	Phosphate rock	0.5	19.65	20.35	40.00
Phosphate rock 452	Phosphate rock	1.0	16.25	19.15	35.40
Phosphate rock 1160	Phosphate rock	1.6	14.70	23.60	38.30
Phosphate rock 451	Phosphate rock	2.2	8.15	23.50	31.55
Tenn. phosphate rock, B14	Phosphate rock	3.4	10.00	20.60	30.60
CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	None	0	23.30	21.25	44.55
CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	CaF <sub>2</sub>	1.0	25.60	21.65	47.25
CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	CaF <sub>2</sub>	3.0	22.35	21.80	44.15
CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	CaF <sub>2</sub>	5.0	24.60	22.10	46.70
CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	CaF <sub>2</sub>	10.0	25.35	21.95	47.30
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	None	0	21.55	20.30	41.85
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	CaF <sub>2</sub>	1.0	23.25	21.00	44.25
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	CaF <sub>2</sub>	3.0	23.10	21.70	44.80
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	CaF <sub>2</sub>	5.0	23.20	20.55	43.75
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	CaF <sub>2</sub>	10.0	22.25	22.10	44.35
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	NaF	1.0	21.20	19.80	41.00
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	NaF	3.0	20.95	23.05	44.00
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	NaF	5.0	21.65	24.30	45.95
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	NaF	10.0	21.55	22.20	43.75
CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	NaF	10.0	26.00	23.70	49.70

\* No nitrogen or potassium added.

added at rates equivalent to 0.3 gm. P<sub>2</sub>O<sub>5</sub> per jar, and ammonium sulfate and potassium chloride were added at the rate of 300 pounds per acre. Sudan



grass was seeded February 27, 1933, and cuttings were harvested on May 2 and June 5, 1933. The treatments and yields of Sudan grass are given in table 10. All jars except the first treatment received nitrogen and potassium fertilizers. The stubble was top-dressed with an equivalent of 300 pounds per acre each of ammonium sulfate and potassium chloride after the cutting made May 2. In the first cutting, differences were apparent in the size of plants growing in soil fertilized with the phosphate rocks containing fluorine. The largest plants were growing in the soil containing the rock with the smallest amount of fluorine. From this there was a gradual decrease in size of the plants as the percentage of fluorine in the phosphate rock increased. The differences were not so pronounced in the second cutting. There were no apparent undesirable effects where soluble fluorine salts were added to the soil.

The results show definitely that the addition to soils of fluorine compounds alone up to 10 p.p.m. of fluorine had no injurious effects on plant growth. Slight differences in the production of dry matter with some treatments can be attributed to plant variation, but in most instances larger concentrations of the same compound did not produce any injury.

The addition of fluorides with mono- and tribasic calcium phosphates did not depress the growth of the plants.  $\text{CaF}_2$  was used as the standard fluorine treatment because it is present in rock phosphate or may result from the decomposition of rock phosphate. The other treatments are supplementary. If anything, there seemed to be a light stimulation in some treatments in the production of dry matter where the fluorides were added. Tri-calcium phosphate produced almost as much, or as much, dry matter as monocalcium phosphate when fluorides were also added to the soil.

The presence of chemically combined fluorine in phosphate rocks greatly affected the availability of the phosphorus to the plants. The availability of the phosphate decreased as the fluorine content of the rock increased. The effect is more apparent in the first crop. As a result of some readjustment in the soil or of the plant's becoming adjusted to different environmental conditions, these compounds are more efficient in producing dry matter in the second crop.

There is a definite relation between the fluorine content of the different phosphate rocks and of basic slag and the total amount of dry matter produced. The correlation factor between the milligrams of fluorine contained in the phosphate added to the soil and the total weight of dry matter produced was  $-.895$ . The odds are 99 to 1 that as the fluorine content of the rock phosphate increased the amount of dry matter decreased. In the studies made, the evidence is conclusive that the efficiency of the phosphorus in producing growth of plants was associated with the fluorine content of the rock phosphate. Moreover, a correlation factor of  $.7967$  between the percentage of citrate-soluble phosphorus and the percentage of fluorine (table 9) shows significant odds, 19 to 1, that the availability as measured by chemical means is associated with the fluorine content of the rock.



The results of analyses made as previously described to determine the percentage of phosphorus in the plants are given in table 11.

Analyses were made on all the plants from these treatments but because the results of each group of treatments are similar only the results from the plants fertilized with phosphate rocks containing varying amounts of fluorine are included. It is to be regretted that it was not possible to separate the roots from the soil without losing many of the fine rootlets. Consequently no analyses were made to determine the fluorine content of the roots or tops. This would have given an opportunity to study further the possibility of fluorine's being precipitated in the roots.

The results from precipitated tricalcium phosphate as a source of phosphorus adds further to the information showing that this compound is a good source of phosphorus for crops in acid soils.

TABLE 11

*Phosphorus content of Sudan grass grown in Clarksville silt loam with phosphates indicated*

SOURCE OF PHOSPHORUS	AVERAGE PHOSPHORUS CONTENT				
	First cutting	Second cutting	First cutting	Second cutting	Total
	per cent	per cent	mgm.	mgm.	mgm.
None added.....	0.142	0.087	3.20	8.40	11.60
Fluorspar basic slag.....	0.142	0.090	9.05	14.35	23.40
Phosphate rock 943.....	0.125	0.087	26.90	20.35	47.25
Phosphate rock 985.....	0.140	0.098	27.40	19.90	47.30
Phosphate rock 452.....	0.130	0.095	21.05	18.10	39.15
Phosphate rock 1160.....	0.125	0.110	18.35	25.70	44.05
Phosphate rock 451.....	0.137	0.101	11.00	23.55	34.55
Phosphate rock, Tenn.....	0.128	0.101	12.80	20.70	33.50
$\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ .....	0.126	0.103	29.10	22.00	51.10
$\text{Ca}_3(\text{PO}_4)_2$ .....	0.117	0.103	25.20	20.90	46.10

The results show that, as the amount of fluorine added in the fertilizer increases, the amount of phosphorus taken up by the plant decreases. A correlation factor of  $-0.9075$  gives odds greater than 99 to 1 that the relationship is not due to chance occurrence and shows that this relationship is specific for the phosphate rocks studied.

The results show very conclusively that the total amounts of dry matter produced and the total amounts of phosphorus absorbed from the phosphate rocks were intimately associated with their fluorine content. This would seem to be nothing more than a direct result of the solubility of the phosphorus in the phosphate rock. However, when the correlation is calculated separately for the first and second cuttings it is found that only in the first cutting is there a highly significant correlation between the fluorine content of the phosphate rocks and the yields of dry matter and the amounts of phosphorus absorbed. Moreover, the results from the second cutting not only show no correlation

between the production of dry matter and phosphorus absorbed with the fluorine added but in five out of seven treatments with phosphate rocks at least as much dry matter was produced as from monocalcium phosphate. In addition the amounts of phosphorus absorbed by the plants were in two cases larger than, in two about the same as, in two slightly less than, and in one considerably less than from monocalcium phosphate. However, in five out of seven treatments, the amount of phosphorus absorbed was as great as, or greater than, within limits of error, that absorbed from tricalcium phosphate. Moreover, more phosphorus was absorbed in the second cutting than in the first from those soils fertilized with samples 1160, 451, and Tennessee, whereas with monocalcium and all other phosphates, appreciably less phosphorus was absorbed by the plants of the second cutting.

The increased absorption can be explained in part as the result of increased root development, giving the plant a larger feeding area. This, however, does not explain the fact that the increases in phosphorus absorbed by the second cutting occurred where the phosphate rocks contained the larger percentages of fluorine and the smaller percentages of their phosphorus in a citrate-insoluble form. Since the production of dry matter and the absorption of phosphorus in this experiment were specifically associated with the fluorine content of the phosphate rocks it seems that some factor other than increased root development is responsible for the differences noted in the uptake of phosphorus in the second cutting. It is hoped that future experiments will aid in the solution of this problem.

#### SUMMARY

Experiments were conducted to study the effect of soluble fluorine compounds on the germination of seeds and the growth of plants. The influence of fluorine on the availability of phosphorus to plants was also studied.

Concentrations of fluorine as large as 50 p.p.m. did not seem to decrease significantly the germination of Sudan grass, cowpea, soybean, red clover, or white Dutch clover seeds. In fact, the germination of white Dutch clover was greatly enhanced by the presence of calcium fluoride and sodium fluosilicate.

The addition of soluble fluorides up to 10 p.p.m. fluorine did not materially decrease the amounts of dry matter produced by cowpeas grown in culture solution. The variations noted were attributed to variations in the plants.

Fluorine in the plants was found largely in the roots. Only when the amounts of fluorine in the roots were relatively large was fluorine present in the tops.

A general trend for the percentage phosphorus in the tops to decrease as the percentage of fluorine in the roots increased was noted and an explanation suggested.

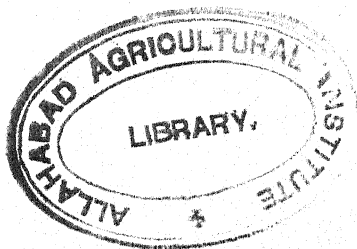
The addition of soluble fluorine compounds to the soil did not seem to affect the availability of the phosphorus in the soil or that added as monocalcium phosphate.

The presence of fluorine in naturally occurring phosphate rocks greatly influenced the availability of their phosphorus to plants. A specific correlation was found between the total amounts of dry matter produced by Sudan grass grown in an acid silt loam soil and the milligrams of fluorine added to the soil in the phosphate rocks studied. There was also a specific correlation between the milligrams of phosphorus found in the plants and the milligrams of fluorine added to the soil in the phosphate rocks.

Evidence is given to substantiate the theory that the availability of the phosphorus in rock phosphate is largely a matter of the rate of solution of the rock phosphate. It is also suggested that the availability to plants of the phosphorus in phosphate rock is associated with the percentage of fluorine in the phosphate rock.

#### REFERENCES

- (1) Aso, K. 1903 On the action of sodium fluoride upon plant life. *Bul. Col. Agr. Tokyo Univ.* 5: 187-196.
- (2) Aso, K. 1903 On the action of sodium silico-fluorid upon plants. *Bul. Col. Agr. Tokyo Univ.* 5: 197-198.
- (3) BARTHOLOMEW, R. P. 1928 The unavailability of phosphorus in rock phosphate to some southern crops. *Jour. Amer. Soc. Agron.* 20: 913-920.
- (4) BARTHOLOMEW, R. P., AND JANSSEN, GEORGE 1929 The relation between concentrations of potassium in culture solutions and optimum plant growth. *Soil Sci.* 27: 189-203.
- (5) COMEY, A. M., AND HAHN, D. A. 1921 A Dictionary of Chemical Solubilities, Inorganic. The MacMillan Co., New York.
- (6) DENIGÉS, G. 1920 Reaction de coloration extrêmement sensible des phosphates et des arseniates. Ses applications. *Compt. Rend. Acad. Sci. [Paris]* 171: 802-804.
- (7) FOSTER, M. D. 1933 Colorimetric determination of fluoride in water using ferric chloride. *Indus. and Engin. Chem. Analyt. Ed.* 5: 234-236.
- (8) GAUTIER, A., AND CLAUSMAN, P. 1916 Le Fluor dans le règne végétal. *Compt. Rend. Acad. Sci. [Paris]* 162: 105-112.
- (9) GAUTIER, A., AND CLAUSMAN, P. 1919 Action des fluorures sur la végétation. B. Cultures en champ. d'expériences. *Compt. Rend. Acad. Sci. [Paris]* 169: 115-122.
- (10) JACOB, K. D., HILL, W. L., MARSHALL, H. L., AND RADER, L. F., Jr. 1933 The composition and distribution of phosphate rock with special reference to the United States. U. S. Dept. Agr. Tech. Bul. 364.
- (11) MAZÉ, P. 1919 Recherche d'une solution (purement minérale) capable d'assurer l'évolution complète du maïs cultivé à l'abri des microbes. *Ann. Inst. Pasteur* 33: 139-173.
- (12) WILLARD, H. H., AND WINTER, O. B. 1933 Volumetric method for determination of fluorine. *Indus. and Engin. Chem. Anal. Ed.* 5: 7-10.
- (13) WILSON, L. B. 1933 Effects of chlorine, bromine, and fluorine on the tobacco plant. *Jour. Agr. Res.* 46: 889-899.
- (14) WÖBER, A. 1920 Über die Giftwirkung von Arsen-Antimon-und Fluorverbindungen auf einige Kulturpflanzen. *Angew. Bot.* 2: 161-178.





# THE EFFECT OF NITROGEN CONTENT OF RYE ON ITS RATE OF DECOMPOSITION

W. B. ANDREWS

*Mississippi Agricultural Experiment Station*

Received for publication October 4, 1934

The rate of decomposition of organic matter in soils under aerobic conditions is greatly influenced by its nitrogen content. Investigations concerning the effect of percentage nitrogen of organic matter on the rate of decomposition with which the writer is acquainted have been made using materials of different kind or of the same kind but of different age.

In an experiment in the greenhouse involving the growth of rye with and without Austrian winter peas with the addition of varying amounts of nitrate of soda, rye was obtained which varied in nitrogen content from 0.64 per cent to 1.83 per cent. The availability of this material afforded an opportunity to determine the effect of the nitrogen content of rye on its rate of decomposition in the soil as measured by the rate of evolution of  $\text{CO}_2$ . This study, therefore, involved a comparison of plant materials of the same kind and age, but not necessarily at the same stage of maturity.

The soil used was a mixture of 10 per cent Houston clay and 90 per cent Oktibbeha fine sandy loam. The Oktibbeha fine sandy loam was very unproductive, whereas the Houston clay was fertile and very high in available phosphorus. The Houston clay was added to supply a good flora and available phosphorus. Two grams of air-dried rye was mixed with 201 gm. of air-dried soil containing 0.55 per cent water, and 30 cc. of water was added. The soil was then crumbled to distribute the water evenly throughout the sample. The water content was comparable to that of a field soil that contains the requisite amount of water to plow well and leave the soil in good tilth.

Then the soil was put into 1,000-cc. Erlenmeyer flasks. The flasks were closed with a 2-hole rubber stopper carrying a long glass tube extending to the bottom of the flask and a short glass tube extending just through the stopper. Glass wool was put over the end of the short tube inside the flask to keep the soil out of it. The flasks were made air-tight by putting over the outer ends of the tubes rubber tubes closed at one end with pointed glass stoppers. Then the flasks with their contents were inverted in their support and maintained at room temperature. The experiment was started on April 5, 1933, and the carbon dioxide was determined on the dates indicated in table 1. When the  $\text{CO}_2$  determinations were made, the flasks were connected in a gas train. The members of the train in order were: soda lime column, soil flask,  $\text{H}_2\text{SO}_4$  tube,

TABLE 1  
*Effect of the nitrogen content on the rate of decomposition of rye as measured by carbon dioxide evolution*

NITROGEN IN RYE†		MILLIGRAMS OF CO <sub>2</sub> EVOLVED PER 24 HOURS FROM THE RYE											TOTAL
		April 5-7	April 7-8	April 8-9	April 9-11	April 11-14	April 14-18	April 18-25	April 25- May 8	May 8- June 1	June 1- June 28	June 28- Aug. 2	
<i>per cent</i>													
0.64	126	85	62	42	28.0	15.8	13.7	9.3	6.46	4.56	2.51	1216	
0.83	138	98	71	48	29.3	16.5	14.9	10.9	7.67	5.37	2.31	1351	
0.83	130	112	70	47	28.7	17.0	14.1	8.5	6.08	4.33	2.09	1236	
1.03	162	125	85	57	34.0	18.8	15.6	10.2	6.92	4.22	1.57	1400	
1.04	161	124	84	56	35.0	19.3	16.1	10.1	7.29	4.26	1.20	1400	
1.11	154	129	87	57	34.3	18.8	16.3	10.4	7.67	4.11	0.91	1394	
1.26	170	144	97	63	37.3	21.3	17.0	11.5	6.67	2.63	1.03	1438	
1.26	178	165	103	66	37.3	18.8	15.7	8.9	4.58	1.70	0.40	1341	
1.31	182	175	111	69	41.0	21.8	17.6	10.8	6.54	2.78	0.80	1522	
1.41	165	169	105	67	42.0	22.5	18.1	11.5	3.71	2.30	1.09	1421	
1.50	180	188	111	71	41.7	22.8	18.4	10.5	5.13	2.63	0.80	1506	
1.83	185	238	135	80	42.0	23.8	17.7	7.3	4.17	2.11	0.51	1519	
Check.....	14.5	9.50	8.80	5.85	5.13	3.45	2.69	2.26	2.33	2.23	1.69	312	
Correlation coefficient	.890± .0627*	.978± .0130	.983± .0103	.983± .0099	.927± .0422	.943± .0332	.880± .0681	-.205± .2888	-.667± .1673	-.826± .0956	-.853± .0823		

\* Standard error.

† The nitrogen determinations were done by Marvin Gieger, experiment station chemist.

CaCl<sub>2</sub> tube, ascarite tube, CaCl<sub>2</sub> tube, and a 3,600-cc. water bottle from which the water was siphoned in order to draw air through the train. The soil flasks were so connected that the air entered them through the long tube and passed downward, finally passing through the soil and out through the short tube, thus facilitating the removal of the carbon dioxide. The carbon dioxide was swept out of the soil flask by drawing 3600 cc. of CO<sub>2</sub>-free air through the train. The CO<sub>2</sub> was absorbed by the ascarite and determined by weighing the tube before and after the absorption.

The data are reported in table 1. The soil microorganisms require nitrogen as well as other nutrients, and the quantity of nitrogen consumed by the soil microorganisms in the decomposition of the rye is very probably directly proportional to the quantities of rye decomposed as measured by the carbon dioxide evolved. The correlation coefficients obtained during the first month of the test are positive and nearly 1, which indicates almost perfect correlation between the percentage of nitrogen in rye and the rate of decomposition of rye. After one month the correlation coefficients become negative and at the last determination during the fourth month the coefficient of correlation was  $-.853 \pm .0823$  (standard error) which means that the decomposition of rye at that stage is inversely proportional to its nitrogen content. Soil microorganisms draw upon the soil for nitrogen to build their bodies when the organic material being decomposed is low in nitrogen. The rye with a higher nitrogen content will require less soil nitrogen in the early stages of decomposition because that liberated by the decomposed rye will be used, and more nitrogen will be liberated by the rye of high nitrogen content. In the later stages of the experiment the rye of low nitrogen content was decomposing at a more rapid rate, which indicates that larger quantities of nitrogen would be tied up in the microorganisms.





# SOME CHEMICAL AND BIOLOGICAL CHANGES PRODUCED IN A FOX SANDY LOAM BY CERTAIN SOIL MANAGEMENT PRACTICES<sup>1</sup>

L. S. CARTER<sup>2</sup>

*Michigan Agricultural Experimental Station*

Received for publication October 17, 1934

The effects of cropping systems and fertilizer and lime applications on soils under experimental conditions have been measured chiefly in terms of differences in plant yields. In some cases changes in the organic matter content of the soil have been measured, and frequently the quantities of available plant nutrients in the soil of treated and untreated plats have been determined. Changes in the biological conditions in soils, however, such as nitrifying power, numbers of bacteria and fungi, and carbon dioxide production, resulting from soil treatments have been studied to a less extent.

In 1917, the Soils Section of Michigan Experiment Station placed under experimental treatment a field of Fox sandy loam soil which had fallen to such a low state of fertility that it had been uncropped for several years. During the succeeding years many of the treated plats attained a fairly high state of fertility as measured by crop yields, as much as 50 bushels of wheat to the acre having been grown on some plats. Marked differences occurred, however, in the crop yields obtained from plats receiving different treatments.

This investigation was carried on to determine to what extent certain chemical and biological changes had taken place in the soil of the plats receiving different treatments, and to find what correlation might exist among the various data collected.

## REVIEW OF LITERATURE

Literature dealing with the relationships of chemical and biological activities in soil and the crop producing power of the soil has been thoroughly reviewed elsewhere (9, 10), and hence no review of the literature is included in this paper.

## EXPERIMENTAL

### *Record of soil treatment and cropping history of plats selected for the investigation*

For the purposes of this investigation eight plats were selected from the experimental field.

<sup>1</sup> A thesis presented to the faculty of the Michigan State College in partial fulfillment of the requirements for the degree of doctor of philosophy. Published, with the approval of the Director, as Journal Article No. 190 n.s. of the Michigan Agricultural Experiment Station.

<sup>2</sup> The writer expresses his sincere appreciation to Dr. C. E. Miller for assistance throughout the course of this investigation.

As the Fox sandy loam is a strongly acid soil, an application of 3 tons of ground limestone to the acre was made at the beginning of the field experiment to all except the check plats. Fertilizers were applied at the following rates per acre: potassium, 100 pounds 50 per cent KCl; nitrogen, 100 pounds  $\text{NaNO}_3$ ; phosphorus, 200 pounds 16 per cent superphosphate; rock phosphate, 1,000 pounds; gypsum, 86 pounds. All of the fertilizers were applied before the crops were planted, with the exception of nitrogen for fall seeded grain. Of this, 40 per cent was applied in the fall, and 60 per cent in the spring until 1920, when the proportions were changed to 20 per cent in the fall and 80 per cent in the spring. Periodic applications of the fertilizers were made as shown in table 1, and according to the amounts already given.

The cropping history of these plats since they have been under experimentation is as follows: soybeans, 1917; rye, 1918; wheat, 1919; sweet clover, 1920,

TABLE 1  
*Periodic application of fertilizers to the designated plats*

SOIL		YEAR OF APPLICATION										
Number	Field* treatment	1917	1918	1919	1922	1923	1924	1926	1927	1928	1929	1930
301N	None	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
301S	Lime	L	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
302	LNPK	LNPK	N	PN	PNK	N	PNK	P	N	PNK	NP	N
305	LPK	LPK	....	P	PK	....	PK	P	....	PK	P	....
307	LN	LN	N	N	N	N	N	....	N	N	N	....
308	LK	LK	....	....	K	....	K	....	....	K	....	....
309	LP	LP	....	P	P	....	P	P	....	P	P	....
310	LRP.C	LRP.C	....	....	RP.C	....	....	....	....	RP.C	....	....

\* L = Lime in the form of ground limestone; K = Potassium as potassium chloride; RP. = Phosphorus as rock phosphate; N = Nitrogen as sodium nitrate; P = Phosphorus as superphosphate; C = Calcium sulfate as gypsum. This legend applies throughout this paper.

1921; rye, 1922; corn, 1923; wheat, 1924; sweet clover, 1925; soybeans, 1926; wheat, 1927; corn, 1928; oats, 1929; and wheat, 1930, 1931. The soybean crop in 1926 was plowed under to supplement the organic matter derived from crop residues. The yield was determined before the crop was plowed under. Other crops were removed, no straw, stover, or similar material being added to the soil.

#### *Method of taking soil samples*

Soil samples of sufficient quantity for all the laboratory studies were taken from the plats in the fall of 1931.

For a representative composite sample, five samples were taken at systematically located points on each plat and thoroughly mixed. Samples were taken by removing and discarding the surface inch of soil and then taking with

a spade the desired amount of plowed soil to a depth of 6 to 8 inches. After thorough mixing and screening to remove stones and large particles of undecomposed organic matter, aliquots were taken, air dried, and stored in sterilized containers.

### *Laboratory methods*

Nitrogen was determined by the method given for soils in the Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists (1). Loss on ignition was determined as a rough measure of organic content, since the soils contained no carbonates. The reaction, in terms of pH, was determined on air-dry soil by the quinhydrone method as described by Bauer (2). Available phosphorus in pounds per acre was obtained by the method of Truog (5). Fred and Waksman's (3) reduction method was used

TABLE 2

*Chemical analyses of soils and crop yields in pounds per acre and in per cent based on the results from the untreated soil, in relation to soil treatment*

SOIL		REACTION	CROP YIELDS		AVAILABLE P <sub>2</sub> O <sub>5</sub>		TOTAL NITROGEN		IGNITION LOSS	
Number	Field treatment	pH	Pounds of dry matter	Per cent	Pounds per acre	Per cent	Pounds per acre	Per cent	Pounds per acre	Per cent
301N	No treatment	4.71	8,857	100	23	100	1380	100	34,200	100
301S	Lime	5.15	26,399	298	26	112	1300	94	35,600	104
302	LNPK	5.59	42,253	478	33	144	1420	103	41,200	120
305	LPK	5.45	37,425	423	34	148	1420	103	41,400	121
307	LN	5.67	32,738	370	29	126	1200	87	36,200	106
308	LK	5.74	29,288	331	30	131	1220	89	36,600	107
309	LP	5.61	25,692	290	32	139	1200	87	34,600	101
310	LRP.C	5.59	27,363	309	40	174	1120	81	34,000	100

to determine nitrate nitrogen. Numbers of bacteria and fungi were obtained by taking the average count from six agar plates of the respective media used. Nitrification and carbon dioxide production methods are described in the respective studies dealing with these substances.

### RELATION BETWEEN SOIL TREATMENT, CROP PRODUCTION, SOIL REACTION, AND SOME AVAILABLE NUTRIENTS

Because of the influence of seasonal variations on crop production, which tend to modify differences due to fertilizer treatment and other factors affecting productivity, it was deemed advisable to express the yields of the different plats in terms of pounds of dry plant material produced during the entire period they have been under experimentation. Table 2 presents a comparison between crop yield and soil reaction, quantities of available phosphorus, loss on ignition, and nitrogen.

Although the supply of available phosphorus is low in all the soils, those receiving phosphate applications have the largest amounts. This is especially true of soils 310N and 309, which were treated with rock phosphate and superphosphate, respectively. Since the available supply of phosphorus is low, any difference due to soil treatment may be expected to have a marked influence on the chemical and biological conditions in these plats.

The soils receiving combinations of lime, nitrogen, and phosphorus were higher in nitrogen and loss on ignition than those receiving lime and single element treatment. Since all the soils were comparatively low in nitrogen and organic matter, additions of these substances should have some effect on the biological activities in these soils.

The data show that lime raised the pH over that of the untreated soil, but not so much as did lime and fertilizers together. Though the differences in reaction between soils receiving lime alone, no treatment, and lime plus fertilizer are appreciable it is doubtful if the differences in reaction between soils receiving different combinations of lime and fertilizers are large enough to have any appreciable effect on the biological and chemical relationships in the soil.

All of the field treatments have increased the yield of crops over those from the untreated soil. Lime alone has given a very marked increase, and lime with combinations of nitrogen, phosphorus, and potassium has given the greatest increases. Combinations of lime and either superphosphate or rock phosphate have shown the smallest increases in crop yields over the untreated soil, the crop yields being about the same as, or slightly greater than, those from lime alone.

#### NUMBERS OF BACTERIA AND FUNGI IN RELATION TO SOIL TREATMENT AND SOME AVAILABLE NUTRIENTS

If available nutrients and numbers of microorganisms in soils are related and are equally affected by soil treatment, as stated by Waksman (9), then a determination of the number of the more important groups of microorganisms and the quantities of available nutrients should show some definite relationships for these soils. The number of fungi developing on acid agar media and of bacteria developing on Brown's albuminate agar media from air-dry samples of the different soils were determined. The results given in table 3 and figure 1 show the actual numbers of organisms present and also the numbers as per cent based on the number found in the untreated soil. The curves are constructed from the percentage data.

Lime alone greatly increased the number of bacteria over the number found in the untreated soil, and lime in combination with fertilizing elements enhanced this increase. This increase in numbers was especially marked for those soils receiving phosphorus with lime or with lime and other fertilizing elements. The evidence points to the important part played by phosphorus in bacterial development in these soils.

All field treatments increased the number of fungi developing on agar plates over that from untreated soil. This increase was exceedingly great for soils 308 and 309, which received lime plus potassium and lime plus superphosphate, respectively. Additions of lime alone, lime plus nitrogen, lime plus rock phosphate, and combinations of lime, phosphorus, and potassium gave only small increases in numbers of fungi in the soil. These results indicate no consistent relationship between soil treatment and number of fungi present.

TABLE 3  
*Numbers of bacteria and fungi in relation to soil treatment*

SOILS		MICROÖRGANISMS			
Number	Treatment	Bacteria		Fungi	
		Number	Per cent	Number	Per cent
301N	None	567,000	100	347,000	100
301S	Lime	1,388,000	245	443,000	128
302	LNPK	1,659,000	293	624,000	180
305	LPK	2,028,000	358	444,000	128
307	LN	1,725,000	305	433,000	125
308	LK	1,614,000	285	905,000	261
309	LP	1,902,000	336	964,000	277
310N	LRP.C	1,917,000	338	438,000	126

TABLE 4  
*Rate of nitrification of urea and several ammonium salts by one of the soils studied*

SOIL TREATMENT	NO <sub>2</sub> NITROGEN END OF 4TH WEEK	NO <sub>2</sub> BASED ON RESULT FOR CHECK
	mgm.	per cent
Check.....	3.28	100
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .....	5.84	178
NH <sub>4</sub> Cl.....	1.95	60
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> .....	10.41	318
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .....	11.28	344
NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .....	10.11	308
(NH <sub>4</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> .....	10.48	320
(NH <sub>4</sub> ) <sub>2</sub> CO.....	11.68	357

A comparison of bacterial numbers and available nutrients shows a distinct relationship between the supply of available phosphorus and numbers of bacteria, except in case of soil 310N. Loss on ignition correlates well with the number of bacteria, except for soils 309 and 310N. Total nitrogen content shows the same correlation with numbers of bacteria as does loss on ignition except in the case of soil 301N. Numbers of fungi showed little relation to soil treatment, soil reaction, or content of available phosphorus, total nitrogen, or loss on ignition.



## NITRIFICATION OF NITROGENOUS MATERIALS IN SOILS AND ITS RELATION TO OTHER SOIL PROCESSES

Nitrification is considered by some investigators as a true measure of soil productivity, since the conditions most favorable for the nitrifying process are very similar to those for plant growth. If this be true or partly so, a study of nitrification in these soils should give some information of value in determining the changes taking place in soils due to soil treatment.

To determine the most suitable materials for nitrification studies in these soils, urea and a group of organic and inorganic salts of ammonium were selected for a preliminary trial on one of the soils used in this investigation. The materials were added in sufficient quantities to give 50 mgm. of nitrogen per 100 gm. of air-dried soil. No attempt was made to determine the most suitable quantity of nitrogen, because several investigators have shown that 30 to 50 mgm. of nitrogen per 100 gm. of soil is well suited for nitrification studies. A sufficient number of soil samples were prepared to permit of determining nitrate production at weekly intervals. The data given in table 4 show only the nitrates found at the end of the 4-week period.

More nitrates were produced from urea and all the salts except ammonium chloride, than from the soil's own supply of nitrogen. Ammonium sulfate was also a poor source of nitrifiable nitrogen. This decrease in nitrification with the addition of ammonium chloride and the relatively slow nitrification of ammonium sulfate is in agreement with the results of Kulik (4) and Turchin (7). Urea was the most rapidly nitrified of the materials used, followed closely by the organic salts of ammonium. Diammonium phosphate was not nitrified rapidly during the first week, but at the end of 20 days it was well nitrified.

For the next study, urea and diammonium phosphate were selected, because the former consistently produced the greatest amounts of nitrates and because the latter produced sufficient quantities of nitrates for the purposes of the study and in addition the phosphate factor was eliminated for all plot treatments. To these were added ground alfalfa and cottonseed meal in order to have a greater variety of materials, since it is maintained (8) that a better picture of nitrification in soils can be obtained by using several materials and more than one method of procedure. The materials were added to 100 gm. of air-dried soil in quantities to give 50 mgm. of nitrogen for urea and diammonium phosphate and 0.5 per cent of the organic plant materials. The usual soil tumbler method was followed throughout the study of nitrification.

Nitrate production from the four applied materials, in milligrams and in per cent based on results for the untreated soil, are given in table 5. Loss on ignition, available phosphorus, and total nitrogen content of the soils on a percentage basis are also included. It is evident from the data that field treatment has changed the ability of these soils to nitrify certain nitrogenous materials. The combination of lime, phosphorus, and potassium in soil 305 has resulted in the greatest nitrification power, followed closely by lime, phos-

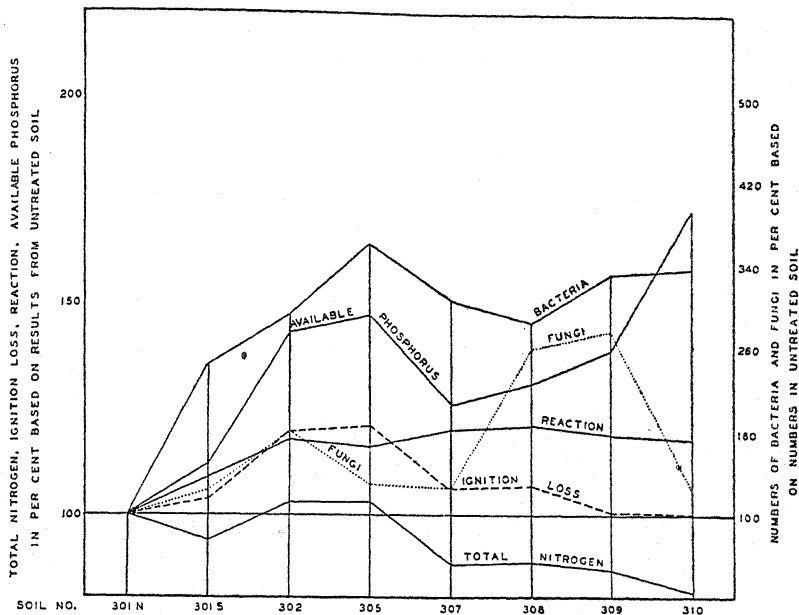


FIG. 1. NUMBERS OF BACTERIA AND FUNGI IN RELATION TO SOIL TREATMENT, SOIL REACTION, CONTENT OF TOTAL NITROGEN, AVAILABLE PHOSPHORUS, AND IGNITION LOSS

TABLE 5

*Nitrate production from different materials in relation to field treatment of soils and to loss on ignition, total nitrogen, and available phosphorus content*

SOIL		NITRATE NITROGEN AT END OF 28-DAY PERIOD IN MG. PER 100 GM. OF SOIL AND IN PER CENT BASED ON RESULT FOR UNTREATED SOIL									LOSS ON IGNITION, AVAILABLE P, AND TOTAL N IN PER CENT BASED ON RESULT FOR UNTREATED SOIL		
Number	Field treatment	Alfalfa		Cotton seed meal		$(\text{NH}_4)_2\text{HPO}_4$		$(\text{NH}_2)_2\text{CO}$		Average for all treatments	Available P	Loss on ignition	Total N
		mgm.	per cent	mgm.	per cent	mgm.	per cent	mgm.	per cent	per cent	per cent	per cent	per cent
301N	None	3.27	100	5.35	100	2.55	100	8.40	100	100	100	100	100
301S	Lime	4.43	135	8.45	158	4.43	173	10.35	123	147	112	104	94
302	LNPK	5.40	165	10.40	195	6.60	259	12.98	155	194	144	120	103
305	LPK	6.00	183	12.50	234	7.28	285	14.43	172	218	148	121	103
307	LN	5.04	155	10.20	191	6.88	270	11.25	134	187	126	106	87
308	LK	4.92	150	11.40	213	6.53	256	11.75	140	189	131	107	89
309	LP	4.80	147	11.30	211	6.90	270	11.59	138	191	139	101	87
310	LRP.C	3.65	112	9.10	170	5.35	238	9.28	111	180	174	100	81

phorus, nitrogen, and potassium in soil 302. Lime plus superphosphate, lime plus potassium, and lime plus nitrogen produced, in the order given, greater quantities of nitrates than lime plus rock phosphate or lime alone. Of impor-

tance is the relatively low nitrifying capacity of the soil receiving no field treatment, which indicates a raising of the nitrifying capacity, for the materials studied, of the other soils through lime and fertilizer treatment.

A close correlation is observed for nitrification of urea and cottonseed meal and for alfalfa meal and diammonium phosphate. The first two materials were nitrified to a greater extent during this period than the latter two. Although there is a difference in rate at which any soil nitrifies these materials, the relationship between soil treatment and nitrification of all of them is similar enough to permit of taking an average of the results for the four materials on a percentage basis for a comparison with other soil factors.

With the exception of soil 310N, which is high in available phosphorus and relatively low in nitrifying capacity for urea and cottonseed meal, there is a close correlation between available phosphorus and nitrate production. Nitrification of alfalfa meal correlates closely with available phosphorus, except for soils 309 and 310, which are high in this element and relatively low in nitrate production from this material. Nitrate production from diammonium phosphate shows little correlation with available phosphorus.

Loss on ignition and nitrate production from cottonseed meal and urea show a clear correlation, but nitrate production from alfalfa and diammonium phosphate shows less relationship.

Total nitrogen shows a similar relation to nitrate production from the different materials, as does loss on ignition.

#### CARBON DIOXIDE PRODUCTION FROM CELLULOSE IN RELATION TO SOIL TREATMENT

It has been claimed by some investigators that a measure of carbon dioxide production furnishes a better index of biological activity in soils than any other method yet devised. A measure of carbon dioxide production from decomposable material in the soils under study should indicate, therefore, changes related to soil treatment, if changes of measurable magnitude have taken place. Cellulose was used as the source of energy. It has further been shown that certain elements, namely nitrogen and phosphorus, influence the rate of  $\text{CO}_2$  production from cellulose, and, since these soils are all low in these elements but show differences due to fertilizer treatment, it was deemed advisable to make some determinations in which phosphorus or nitrogen was added with cellulose to the soils. For additional comparisons, potassium and calcium in the form of chlorides were added with cellulose to some cultures. "Ascarite" was used for absorbing the carbon dioxide. The method used is similar to the one found entirely satisfactory for this kind of a study by Turk (6).

Results of carbon dioxide production determinations in milligrams per 100 gm. of soil and in per cent based on results from the untreated soil are given in table 6. A comparison of the milligrams of carbon dioxide produced under the different treatments shows that nitrate nitrogen was most effective in hastening the decomposition of cellulose. These results substantiate conclusions cited in the literature that nitrogen plays a very important part in



cellulose decomposition as measured by  $\text{CO}_2$  production. It bears out the statement made in an earlier part of this paper that these soils being extremely low in total nitrogen would be expected to respond to applications of this element.

Additions of available phosphorus increased the production of carbon dioxide from cellulose much more than did additions of calcium or potassium chloride. This stimulation of carbon dioxide production from cellulose by phosphorus additions follows from the fact that these soils are relatively low in this element and that available phosphorus supply has been shown to influence the rate of cellulose decomposition as measured by  $\text{CO}_2$  production.

Additions of calcium and potassium chlorides increased to a limited extent the production of carbon dioxide from cellulose over that from the soils receive-

TABLE 6

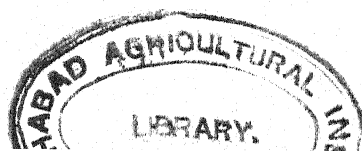
*Carbon dioxide production from cellulose with different chemicals added in relation to soil treatment*

SOIL		CARBON DIOXIDE PRODUCTION IN 24 DAYS										
Number	Field treatment	Cellulose		$\text{CaCl}_2$ + cellulose		$\text{KCl}$ + cellulose		$\text{Na}_2\text{HPO}_4$ + cellulose		$\text{NaNO}_3$ + cellulose		Average for all treatments
		mgm.	per cent	mgm.	per cent	mgm.	per cent	mgm.	per cent	mgm.	per cent	
301N	None	149	100	126	100	130	100	294	100	493	100	100
301S	Lime	169	113	151	120	166	127	231	78	548	111	110
302	LNPK	204	137	213	169	216	166	268	91	619	126	138
305	LPK	223	150	231	183	248	191	286	98	643	130	150
307	LN	171	115	216	171	238	183	263	89	614	124	136
308	LK	171	115	207	164	224	172	250	85	629	127	132
309	LP	158	106	190	151	197	152	243	83	560	114	121
310	LRP.C	122	82	181	144	174	134	214	73	585	118	111

ing cellulose alone. Potassium chloride seemed to be more effective in this respect than calcium chloride.

When the results of carbon dioxide production from cellulose with certain chemicals added is calculated in per cent based on results for the untreated soil, as shown in table 6, the effect of soil treatment on this process may be demonstrated. The results show a marked increase in the soil's ability to produce  $\text{CO}_2$  from cellulose for all fertilizer treatments as compared to the untreated soil. Lime alone increased the production of  $\text{CO}_2$  from cellulose over the untreated soil, but not to the extent that combinations of lime, nitrogen, phosphorus, and potassium did.

The production of  $\text{CO}_2$  from cellulose was greatest in soil 305, which had received lime, potassium, and phosphorus in the field. Soil 302 followed 305 in  $\text{CO}_2$  production from cellulose alone, but combinations of lime plus nitrogen, lime plus potassium, and lime plus phosphorus were little if any better than lime alone in increasing the production of  $\text{CO}_2$  from cellulose in these soils.



The relation between carbon dioxide production from cellulose alone, total nitrogen, and available phosphorus in the soil further emphasizes the importance of these elements, especially nitrogen, in this process. Carbon dioxide production from cellulose with potassium and calcium chlorides added show a close relation to total soil nitrogen for all soils.

#### INTERRELATIONS BETWEEN NITRIFICATION, CARBON DIOXIDE PRODUCTION, BACTERIAL NUMBERS, CROP YIELDS, AND AVAILABLE NUTRIENTS

The previous studies showed that fertilizer treatments produced some chemical and biological differences in the soil under study. It is of interest at

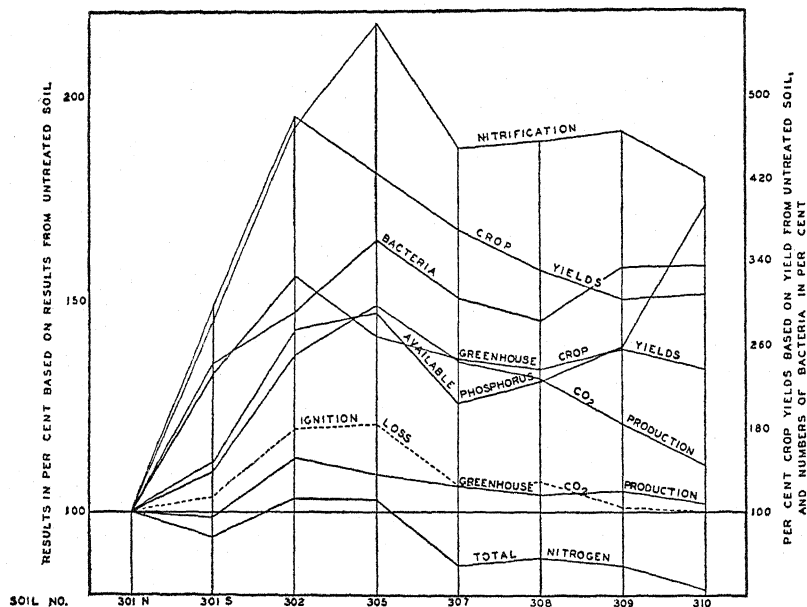


FIG. 2. INTERRELATION BETWEEN NITRATE PRODUCTION, CONTENT OF AVAILABLE PHOSPHORUS, TOTAL NITROGEN, AND IGNITION LOSS, BACTERIAL NUMBERS, CROP YIELDS IN THE FIELD AND GREENHOUSE, AND CARBON DIOXIDE PRODUCTION FROM FIELD AND GREENHOUSE SAMPLES IN SOILS RECEIVING DIFFERENT FIELD TREATMENTS

this time to make a comparison of all the relationships, in order to obtain a better picture of conditions as a whole in these soils. In figure 2 all of the results are presented, expressed in per cent, the data from soil 301N, which received no fertilizer treatment, being used as a basis. For convenience, results from greenhouse studies presented on following pages are included in the figure. These will be discussed later.

Soil 305, treated in the field with lime, phosphorus, and potassium, showed the greatest nitrifying power, carbon dioxide production, number of bacteria, and loss on ignition and ranked second in the production of crops. Soil 302,

treated in the field with lime, nitrogen, phosphorus, and potassium, produced the largest yields of crops but ranked second to soil 305 in loss on ignition, nitrifying capacity, and carbon dioxide production and equalled it in total nitrogen content. The soil treatments in their order of efficiency for maintaining organic content of the soil, as indicated by loss on ignition, were: LPK, LNPK, LK, LN, L, LP, with LRPC and no treatment on a par.

Available phosphorus was proportionately higher in those soils receiving this element in the field than in those receiving lime or combinations of lime and other fertilizing elements. This condition was especially pronounced in soil 310, which received large amounts of rock phosphate. From these results it is evident that the supply of available phosphorus can be increased in these soils by additions of certain forms of this element; especially is this true where large amounts are applied and relatively small amounts are removed by the crops.

Field treatments consisting of lime plus superphosphate and of lime plus rock phosphate and gypsum affected all factors studied, except available phosphorus and bacterial numbers, to a less extent than did any treatment aside from lime alone.

The results as a whole indicate that treatments including combinations of fertilizer elements and lime had a greater effect on all factors studied than did application of the elements singly with lime. Furthermore, in combination with lime no single element was more effective in all respects than were other elements. These data clearly indicate that the soil studied is in need of all three fertilizing elements. The need for potassium and phosphorus is evidently greater than for nitrogen, since the effect of the LPK treatment is equal to or greater than the effect of the LNPK in all respects except crop yield.

#### GREENHOUSE STUDIES

To determine further the effect of soil treatment on chemical composition and biological processes in the soil, crops of sweet clover, rye, and soybeans were grown on the soils in pot cultures in the greenhouse. The crops were cut after a 12-week growth period and air dried, and weights were determined. For carbon dioxide production study, the harvested material was then ground and returned to a portion of the soil on which it had grown. It was the object of this study to determine whether soil differences found in the previous work on these soils could be measured by crop yields in the greenhouse and whether carbon dioxide production, when the crops grown were returned to the soils, was comparable to results from previous carbon dioxide production studies.

Duplicate 2-gallon pots of the different soils were used. The moisture content was maintained by weighing the pots at frequent intervals and bringing up to weight with distilled water. The crop yields in grams and in per cent based on the yield from the untreated soil are given in table 7.

The results show that soil 302, treated in the field with lime, nitrogen, phosphorus, and potassium, produced the largest yields of all three crops and

that soil 305, treated in the field with lime, potassium, and phosphorus ranked second in yield of plant materials. These results are in accord with those obtained under field conditions. Field treatments of lime plus nitrogen, and of lime plus potassium, gave approximately the same yields of leguminous plant material as did lime alone, but the yields were not so large as for soils 302, 305, and those receiving lime with phosphorus. The soil receiving lime alone gave larger yields of all crops in the greenhouse than did the untreated soil, but not so large as soils receiving any combination of fertilizer with lime.

The unusually low yields of all crops on the untreated soil 301N is of special interest as they indicate the low fertility of the soil where no fertilizer treatments have been made. This decrease in ability to produce crops is especially marked for the legumes, where considerable difficulty was experienced in obtaining measurable yields of plant material. Undoubtedly this condition was due primarily to a deficiency of lime.

TABLE 7

*Crop yields from greenhouse pot studies expressed as grams of air-dry plant tissue and in per cent based on results from untreated soil*

SOIL		SWEET CLOVER		RYE		SOYBEANS		AVERAGE
Number	Field treatment							
		gm.	per cent	gm.	per cent	gm.	per cent	per cent
301N	None	1.00	100	15.15	100	6.14	100	100
301S	Lime	4.36	436	16.45	108	9.55	155	233
302	LNPK	6.61	661	22.35	148	10.74	175	328
305	LPK	4.99	499	20.10	133	10.45	170	267
307	LN	4.44	444	19.55	129	9.95	162	245
308	LK	4.37	437	17.80	118	9.70	158	238
309	LP	4.79	479	18.95	125	10.32	168	257
310	LRP.C	4.41	441	16.20	107	10.22	166	236

A definite relation was found to exist between fertilizer treatment of the soils and residual effects on crop production in greenhouse pot tests. In general the variations in yields with different soil treatments was similar for all three crops. The relationship was especially noted for the sweet clover and soybean crops.

#### CARBON DIOXIDE PRODUCTION IN SOIL AFTER ADDITION OF ONE PER CENT PLANT MATERIAL PREVIOUSLY GROWN ON THE SOIL

Samples of soil from the pots used in the greenhouse tests were placed in the aspirating flasks used in the previous experiments for determining carbon dioxide production. The procedure described for the previous study of carbon dioxide production was followed. The results obtained both in milligrams and in per cent based on results from the untreated soil are shown in table 8.

The data show sweet clover to be more readily decomposed than soybeans

or rye. These results are in agreement with those of other workers. The explanation of this relationship has been thoroughly discussed in papers dealing directly with the subject and, hence, will not be repeated.

All soils receiving lime alone or lime plus fertilizer in the field produced more carbon dioxide from sweet clover than did the untreated soil. Likewise all treated soils with the exception of that receiving lime alone produced more carbon dioxide from soybeans than did the untreated soil. On the other hand, only soils 302 and 305 produced as much carbon dioxide from rye as did the untreated soil.

The soil receiving complete fertilizer in addition to lime produced more carbon dioxide from all three materials than did any other soil. This soil also produced the largest crops under both field and greenhouse tests.

A previous study showed marked differences in the power of these soils to produce carbon dioxide from cellulose. Only small differences, however, were

TABLE 8

*Carbon dioxide produced from soils to which had been added plant tissue previously grown on them*

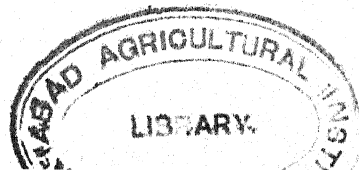
SOIL		SWEET CLOVER		RYE		SOYBEANS		AVERAGE
Number	Field treatment							
		mgm.	per cent	mgm.	per cent	mgm.	per cent	per cent
301N	None	287	100	225	100	252	100	100
301S	Lime	296	103	200	89	262	99	99
302	LNPK	343	120	238	106	283	113	113
305	LPK	323	113	224	100	285	109	109
307	LN	320	111	216	96	282	106	106
308	LK	325	113	200	89	280	104	104
309	LP	309	108	211	94	289	105	105
310	LRP.C	295	103	201	89	286	102	102

found in the capacity of the soils to produce carbon dioxide from plant material grown on them, as indicated by the average results in table 8. It is evident, therefore, that addition of plant tissue, which contains all the nutritive elements, largely eliminates the differences in these soils, arising from previous treatment, to produce carbon dioxide.

A comparison of nitrification, carbon dioxide production, yields of crops, total nitrogen, and greenhouse studies is made in figure 2. Crop yields in the field and greenhouse, and carbon dioxide production from plant material show a close correlation for all soils except soil 309, which gave relatively higher yields in the greenhouse and in carbon dioxide produced from crops grown on it.

Nitrification, carbon dioxide production, both from cellulose and plant tissue, and greenhouse crop yields show a very close correlation in all soils but number 302, which gave relatively higher values in the greenhouse studies.

In general, it may be said that variations in crop producing power, resulting from previous soil treatment, correlate well with results of the studies of biological activities.



## SUMMARY AND CONCLUSIONS

A study was made of changes in some of the more important chemical and biological conditions in a Fox sandy loam soil, resulting from fertilizer and lime applications over a period of 17 years. Particular emphasis was placed on crop production in relation to chemical and biological conditions in the soil and to field treatment.

The results permit of the following conclusions:

Lime plus complete fertilizer and lime plus phosphate and potash were the most effective in increasing the content of volatile matter of the soil and they also increased the nitrogen content, whereas all the other treatments decreased nitrogen content. Lime alone and lime plus individual nutrients increased the loss on ignition slightly.

All soil treatments increased pH values and available phosphorus.

All soil treatments increased crop yields, the lime plus complete fertilizer and lime plus phosphate and potash treatments being the most effective.

All soil treatments increased the number of fungi in the soil and greatly increased the number of bacteria. All fertilizer treatments in addition to lime proved beneficial to bacterial growth.

Nitrifying power of the soil varied greatly with the source of nitrifiable nitrogen. An average of results for alfalfa meal, cottonseed meal, diammonium phosphate, and urea showed that the two plots giving the highest crop yields and containing the largest content of volatile matter and a high content of available phosphorus to have the greatest nitrifying power.

All soil treatments except lime plus rock phosphate and gypsum increased the production of  $\text{CO}_2$  from cellulose. Addition of  $\text{CaCl}_2$  or  $\text{KCl}$  to soils receiving no field treatment decreased  $\text{CO}_2$  production from cellulose, whereas  $\text{Na}_2\text{HPO}_4$  and  $\text{NaNO}_3$  increased it.  $\text{CO}_2$  production in field treated soils, compared to that from untreated soil, was increased by addition of  $\text{KCl}$ ,  $\text{CaCl}_2$ , or  $\text{NaNO}_3$  but decreased by addition of  $\text{Na}_2\text{HPO}_4$ .

Yields of sweet clover, rye, and soybeans grown in jars of the different soils in the greenhouse correlated with yields obtained under field conditions. When the crop material grown on each jar was ground and an aliquot returned to a portion of the soil from the jar,  $\text{CO}_2$  production correlated in general with crop yield.

## REFERENCES

- (1) Association of Official Agricultural Chemists 1925 Official and Tentative Methods, ed. 2. Washington, D. C.
- (2) BAUER, L. D. 1926 The use of the quinhydrone electrode for measuring the hydrogen ion concentration of soils. *Soil Sci.* 21: 167-179.
- (3) FRED, E. B., AND WAKSMAN, S. A. 1928 Laboratory Manual of General Microbiology. McGraw Hill Book Company, New York.
- (4) KULIK, G. 1932. The influence of chlorides and sulphates on the nitrification of nitrogenous fertilizers. *Chem. Abs.* 26: 1698.
- (5) TRUOG, EMIL 1930 The determination of readily available phosphorus of soil. *Jour. Amer. Soc. Agron.* 22: 874-882.
- (6) TURK, L. M. 1931 The composition of soybean plants at various growth stages as related to their rate of decomposition and use as green manure. *Mo. Agr. Exp. Sta. Res. Bul.* 173.
- (7) TURCHIN, F. V. 1932 Transformation of urea in the soil. *Chem. Abs.* 26: 2265.
- (8) WAKSMAN, S. A. 1923 Methods for the study of nitrification. *Soil Sci.* 15: 241-260.
- (9) WAKSMAN, S. A. 1932 Principles of Soil Microbiology, ed. 2. Williams and Wilkins Co., Baltimore.
- (10) WAKSMAN, S. A., AND STARKEY, R. L. 1924 Microbiological analysis of soil as an index of soil fertility. *Soil Sci.* 17: 145-151.



## ABSORBED SODIUM IN SOILS AS AFFECTED BY THE SOIL-WATER RATIO

FRANK M. EATON AND V. P. SOKOLOFF

*Bureau of Plant Industry, U. S. Department of Agriculture<sup>1</sup>*

Received for publication October 17, 1934

Data are presented in this paper that bear on base exchange determinations and base exchange equilibria as affected by the soil-water ratio. The proportions as well as the absolute amounts of constituents found in 1:5 aqueous extracts of soils and in displaced soil solutions are very different. The neglect of this fact has given rise to misleading results in base exchange studies.

In 1928 the attention of one of us was attracted by a lemon grove near Chula Vista, California. This grove, since the time of its planting in 1897, has been irrigated exclusively from a dug well on the property. A water sample collected in 1928 contained 28 m.e. per liter (1,000 p.p.m.) of chloride, which is very high for an irrigation water and higher than any known to be used elsewhere for citrus irrigation. The initial and subsequent water samples from the well have been alike in that sodium has constituted approximately 50 per cent of the bases, magnesium has been a little less concentrated than calcium, and the bicarbonate and sulfate concentrations have been relatively low. The chloride concentration of the water from this well has varied upward from that of the initial sample to a chloride concentration of 44.35 m.e. (1,570 p.p.m.) in August, 1933. The trees in this grove are not in good condition.

Because of the recognition that this grove presented a subject of value in connection with salt-tolerance studies and that the concentration of chlorides in the soil solution of the root zone must at least approach the upper limit of citrus tolerance, soil samples were collected on December 8, 1933. These were taken both from the old grove (sample 239) and from a younger 10-year-old planting (sample 238) containing tangerines, grapefruit, and oranges, as well as lemons. Each of the samples represented the 6-24 inch horizon and was composited from five borings, including both the furrow area and the row centers. After the samples had been taken to the laboratory in moist condition and their moisture content increased with the well water, displacements of the soil solutions were made. Conventional 1:5 extracts were also made for comparison. The latter extracts were of oven-dried aliquots of the soils.

The analyses of these solutions brought to light outstanding differences between the proportions of sodium and calcium in the displaced soil solutions and in the 1:5 extracts (table 1). A much lower proportion of calcium was

<sup>1</sup> Rubidoux Laboratory, Riverside, California.

found in the 1:5 extracts than in the displaced solutions, whereas sodium was much higher in the extracts. These observations prompted further investigations including determinations of adsorbed bases and of the total exchange capacity of these soils. Upon the completion of this study six other soils of lesser salinity were similarly examined. One of these soils was further investigated after being wet with a solution containing about four times as much sodium, commercial NaCl, as there was calcium in the ammonium acetate extract. Five of these soils were from a series collected in 1931 for boron studies. Analyses of 5-times-saturation aqueous extracts of these five soils had been made previous to this inquiry.

The analytical procedures were those used at the Rubidoux Laboratory for water analyses.  $\text{HCO}_3$ , Cl,  $\text{SO}_4$  were determined by the Official A. O. A. C. methods; Ca was determined by the titration of calcium oxalate; Mg, by weighing magnesium pyrophosphate; Na, by weigh-

TABLE 1

*Composition of displaced soil solutions and of 1:5 extracts*

Concentrations are expressed in milligram equivalents per liter. Comparison of the displaced soil solutions and 1:5 extracts has been facilitated by multiplying the latter by appropriate factors which take account of the soil-water ratio, i.e., soil 238 by 27.9 (5/0.179) and soil 239 by 30.3 (5/0.165).

	SOIL- WATER RATIO	MILLIGRAM EQUIVALENTS PER LITER							Sodium
		HCO <sub>3</sub>	Cl	SO <sub>4</sub>	Ca	Mg	K	Na	<i>per cent</i>
Soil 238:									
Displaced sol'n. ....	1:0.179	4.0	285.6	18.2	92.0	76.5	22.2	144.0	49.7
1:5 ext. x 27.9. ....	1:5	22.3	251.9	30.2	43.3	64.2	10.3	205.8	66.8
Soil 239:									
Displaced sol'n. ....	1:0.165	3.8	219.0	14.2	68.8	69.8	6.7	92.4	41.7
1:5 ext. x 30.3. ....	1:5	50.0	179.4	33.6	34.2	59.4	19.1	170.6	67.0

ing uranyl zinc acetate hexahydrate; and K, by weighing di-potassium sodium cobaltinitrite monohydrate. Absorbed ammonia was determined by aeration by the Chapman and Kelley (2) procedure, following details of the method supplied by Dr. Chapman.

The Burd and Martin (1) procedure for the displacement of soil solution was followed, 2 kilos of soil packed in  $2\frac{3}{8}$ -inch displacement tubes being employed. Proebsting's (3) suggestion that the insides of the tubes be greased to prevent channelling was adopted, as was Hibbard's (5) scheme for automatically obtaining successive fractions of the displaced solution. At best, soil-solution displacements are difficult, and for successful displacements some exploratory work must ordinarily be carried out on each soil, such as variations in moisture content, firmness and method of tamping into the displacement tubes, and the amount of air pressure applied during displacement. If like conductances are obtained for several successive 20-ml. fractions of the percolate it is customary to assume that a true displacement has been obtained, but such conclusion may be in error. Channelling and displacement sometimes take place simultaneously at essentially uniform rates with misleading results. A further check on the adequacy of a displacement is accordingly required. The chloride content of an aliquot of displaced solution corresponding to 100 gm. of dry soil should be at least as high as that of a 1:5 extract of a corresponding soil mass. When a greater quantity of



chloride is represented by a displaced solution than by an aqueous extract the writers have concluded that a portion of the soil water has not functioned as a solvent and is not displaced, or, in other words, has behaved as bound water; possibly water of hydration of colloidal soil components. Accordingly, the *effective* soil moisture as represented by the displaced solution may be less than that represented by the moisture content of the soil as determined by drying at 105°C. (See footnote to table 2.) If our deduction with respect to the presence of *bound water* in certain of these soils is valid it would seem most logical to consider in this connection the water of hydration of  $\text{SiO}_2$  and of the absorbed bases, particularly Na.

It has been found impossible to displace the soil solution from some heavy soils except at moisture contents well below the moisture equivalent percentage. If a soil is dispersed or is inclined to lose structure when handled moist it is advantageous to wet it by sprinkling uniformly after spreading to a uniform thickness of 5 mm. on a metal table top. When so spread and sprinkled, the soil is allowed to stand covered with an oilcloth overnight before it is mixed by sieving.

The observations made in the case of the Chula Vista soils were substantially confirmed by the analyses of the six additional soils (table 2). These findings may be stated as follows: *The amount of sodium, both relative and absolute, in the aqueous phase tends to increase as the water-soil ratio is increased, whereas the relative concentration of calcium (and magnesium in some cases) tends to decrease. The absolute amount of calcium in solution may remain unchanged or tend to increase with dilution when soils contain an excess of sparingly soluble salts such as  $\text{CaCO}_3$  or  $\text{CaSO}_4$ .*

This phenomenon cannot be explained on the basis of solubility. On that basis it would be expected that Ca and Mg rather than Na and K would appear in the aqueous phase with dilution, since, with the exception of the chlorides, Ca and Mg salts are less soluble than the corresponding salts of Na and K. It would be equally difficult to explain it as due to the hydrolysis of Na of the absorbing complex, since the concentration of other salts in solution was probably sufficiently high to minimize such hydrolysis. Hydrolysis in the soils examined likewise would fail to account for the disappearance of Ca from the aqueous phase with dilution. *The most satisfactory explanation of this phenomenon is that a cation exchange reaction takes place when the water:soil ratio is increased whereby calcium enters the absorbing complex and sodium is liberated.*

From 4 to 17 times as much bicarbonate (alkalinity to methyl orange reported as bicarbonate) was found in 1:5 extracts as in the displaced soil solutions. As previously stated, it would not be reasonable to connect all of this increase with hydrolysis of the adsorbed Na. Electrometric determinations of pH with a glass electrode (for which we are indebted to L. V. Wilcox) were made only in the case of soil 277. The pH values for the soil:water ratios 1:0.117, 0.154, 0.5, 1.0, 2.5, 5.0, 10.0 were respectively as follows: 7.48, 7.31, 7.60, 7.24, 7.02, 6.97, 6.97. In the case of the remaining soils colorimetric pH determinations did not show significant trends or variations. The increase in  $\text{HCO}_3^-$  was probably due for the most part to the carbonates of Ca and Mg entering the solution. The cations, Ca and Mg, which entered

TABLE 2

*Cations of displaced soil solutions, 5 times saturation extracts, 1:5 extracts, and ammonium acetate extracts*

SOIL NO.	MOISTURE EQUIVALENT	SOIL WATER RATIO	MILLIGRAM EQUIVALENTS PER 100 GM. SOIL									PER CENT OF TOTAL			
			HCO <sub>3</sub>	Cl	SO <sub>4</sub>	Ca	Mg	K	Na	Total bases	NH <sub>4</sub> ab-sorbed	Ca	Mg	K	Na
238*	20.7 <i>per cent</i>	1:01.79	0.06	4.50	0.29	1.45	1.21	0.35	2.27	5.28	.....	27	23	7	43
		1:2.325	0.34	4.48	0.42	0.94	1.12	0.10	3.31	5.47	.....	17	21	2	60
		1:5	0.40	4.51	0.54	0.78	1.15	0.18	3.69	5.80	.....	13	20	3	64
Ammonium acetate extract .....						9.06	7.88	1.02	4.53	22.49	22.31				
239*	23.4	1:0.165	0.05	2.90	0.18	0.92	0.92	0.09	1.22	3.15	.....	29	29	3	39
		1:2.700	0.46	2.84	0.35	0.61	0.71	0.06	2.40	3.78	.....	16	19	2	63
		1:5	0.83	2.96	0.55	0.56	0.98	0.31	2.82	4.67	.....	12	21	7	60
Ammonium acetate extract .....						19.01	10.55	1.11	3.93	34.60	18.59				
2	11.9	1:0.123	0.08	0.13	0.15	0.29	0.09	0.02	0.19	0.59	.....	49	15	3	33
		1:1.565	0.39	0.11	0.15	0.35	0.13	0.05†	0.34	0.87	.....	40	15	6	39
		1:5	0.89	0.13	....	0.50	0.22	0.11	0.43	1.26	.....	40	17	9	34
Ammonium acetate extract .....						36.34	2.43	0.55	0.77	40.09	8.82				
4	11.5	1:0.122	0.14	0.06	0.09	0.17	0.07	0.01	0.09	0.34	.....	50	21	3	26
		1:1.415	0.27	0.07	0.11	0.21	0.11	0.03†	0.19	0.54	.....	39	20	6	35
		1:5	0.59	0.09	....	0.42	0.27	0.04	0.27	1.00	.....	42	27	4	27
Ammonium acetate extract .....						9.04	1.06	0.90	0.99	11.99	8.34				
4A*	....	1:0.124	....	31.69	....	3.89	0.98	0.11	29.84	34.82	.....	11	3	..	86
	1:5	....	31.69	....	2.02	0.64	0.14	32.40	35.20	.....	6	2	..	92	
Ammonium acetate extract .....						8.70	3.65	2.20	32.55	47.10	8.33				
7	22.5	1:0.174	0.06	0.18	0.69	0.45	0.25	0.01	0.30	1.01	.....	45	24	1	30
		1:2.340	0.33	0.15	0.91	0.46	0.27	0.01†	0.69	1.43	.....	32	19	1	48
		1:5	0.57	0.17	0.75	0.48	0.72	0.02	0.81	2.03	.....	24	35	1	40
Ammonium acetate extract .....						15.96	7.06	0.46	1.51	24.99	18.70				

\* On the assumption that all of the chloride of soils 238, 239, and 4A was in solution in the 1:5 extracts, the chloride found in the displaced soil solutions of these soils corresponded respectively to 15.8, 13.5, and 11.4 ml. of water per 100 gm. of soil rather than to the 17.9, 16.5, and 12.3 ml. as represented by moisture determinations on aliquots of the soil as packed. The concentrations of all displaced solution constituents of these three soils accordingly are calculated to 100 gm. of dry soil on the basis of the active water indicated by the chloride determinations.

† Determined by difference in 1931.

TABLE 2—*Concluded*

SOIL NO.		MOISTURE EQUIVALENT	SOIL WATER RATIO	MILLIGRAM EQUIVALENTS PER 100 GM. SOIL								PER CENT OF TOTAL					
				HCO <sub>3</sub>	Cl	SO <sub>4</sub>	Ca	Mg	K	Na	Total bases	NH <sub>4</sub> ab-sorbed	Ca	Mg	K	Na	
9	17.4	per cent															
		1:0.127	0.05	0.35	0.56	0.58	0.36	0.01	0.22	1.17	.....	50	31	1	18		
		1:1.785	0.26	0.31	1.16	0.79	0.49	0.09†	0.58	1.95	.....	40	25	5	30		
		1:5	0.84	0.36	0.98	0.81	0.60	0.07	0.77	2.25	.....	36	27	3	34		
Ammonium acetate extract .....							11.99	5.44	1.11	0.91	19.45	14.79					
10†	21.3	1:0.144	0.04	0.48	1.38	0.38	0.23	0.02	1.41	2.04	.....	19	11	1	69		
		1:2.215	0.43	0.54	2.27	0.31	0.30	....	2.84	3.45	.....	9	9	..	82		
		1:5	0.62	0.55	2.47	0.41	0.30	0.16	3.13	4.00	.....	10	7	4	79		
Ammonium acetate extract .....							10.49	10.06	0.94	5.22	26.71	15.30					
277	16.8	1:0.117	0.07	0.48	0.11	0.24	0.07	Tr.	0.35	0.66	.....	36	11	..	53		
		1:0.154	0.06	0.50	0.10	0.21	0.07	....	0.43	0.71	.....	30	10	..	60		
		1:0.5	0.14	0.44	....	0.14	0.06	....	0.48	0.68	.....	21	9	..	70		
		1:1.0	0.19	0.46	0.18	0.15	0.09	....	0.61	0.85	.....	18	10	..	72		
		1:2.5	0.37	0.48	0.23	0.19	0.11	....	0.79	1.09	.....	17	10	..	73		
		1:5.0	0.57	0.46	....	0.20	0.10	Tr.	0.86	1.16	.....	17	9	..	74		
		1:10.0	0.74	0.48	0.21	0.21	0.14	....	0.95	1.30	.....	16	11	..	73		
Ammonium acetate extract.....							12.45	4.25	1.85	2.31	20.86	12.74					

† Repeated trials for a better displacement of soil 10 at the time of the above work were unsuccessful. Subsequently, by the use of a long 1-inch displacement tube and a conical tamper, a solution was obtained that had a chloride content corresponding to 0.84 m.e. per 100 gm. of soil, indicating 5.0 ml. of bound water per 100 gm. of soil. Channelling to the extent of 43 per cent in the displaced solution of soil 10 as reported in this table is indicated by the 0.84 m.e. of chloride found in this subsequent displacement. This channelling a little more than offsets the bound water, but corrections have not been applied to the data.

In these deductions with respect to bound water, recognition has not been given to the possibility that chloride, at least to a limited extent, may be adsorbed. If chloride was adsorbed in these cases then our bound water estimates are too low.

with dilution as carbonates or bicarbonates, however, replaced in part Na of the absorbing complex and in part remained in solution. The presence in the soil of sparingly soluble salts such as CaCO<sub>3</sub> and CaSO<sub>4</sub> tends to obscure the base exchange effect because the quantity of Ca derived from these salts increases with the proportion of solvent used.

If the energy of absorption of Ca, Mg, K, and Na from aqueous solutions decreases in the order named, calcium should displace sodium to the greatest extent, which is the result observed. In a number of cases appreciable quantities of magnesium appeared in the aqueous phase with dilution. To what extent this magnesium was displaced by calcium or derived by the solution of MgCO<sub>3</sub> is uncertain. The liberation of Mg from the absorbing complex by

Ca displacement should follow, if not accompany, Na displacement, particularly when the concentration of adsorbed sodium is relatively low. In the soils here examined relatively little potassium was displaced by ammonium acetate; the actual and relative amounts were less than of sodium. The relative concentrations of the four bases in the aqueous and solid phases are functions of their energy of absorption and of their thermodynamic activities. Vanselow (7) has assumed the thermodynamic activities of the cations in the solid phase to be equal to their mol fractions, since he considers the solid phase to be a solid solution or mixed crystal.

Two distinct effects are made evident by the data of table 2. Both are important and both simultaneously contribute to the reclamation of calcareous alkali soils when leached with non-saline waters. The first of these effects for convenience may be designated as the *calcium carbonate effect* and the second as the *dilution effect*.

The calcium carbonate effect has come to be generally recognized. Experiments and discussion by Kelley and Brown (6), Gedroiz (4), and others may be referred to. When the soil solution of a calcareous alkali soil is replaced by non-saline water, Ca comes into solution from solid  $\text{CaCO}_3$  and the proportion of Ca in the aqueous phase is thereby momentarily increased. With this increase in the concentration of Ca relative to Na, absorbed Na is replaced and continues to be replaced by more Ca from  $\text{CaCO}_3$  until the Ca and Na of the aqueous phase are in equilibrium with the Ca and Na of the absorbed phase. At equilibrium the aqueous phase is higher in Na than in Ca, since the energy of absorption of the latter is the greater. Reclamation is effected when the cycle has been repeated until Na of the exchange complex has been largely replaced by Ca derived from  $\text{CaCO}_3$ .

The dilution effect as here demonstrated has implications of a broader nature but it likewise contributes to the effectiveness of reclamation by leaching though its significance in this connection seems not to have been elaborated. Dilution of the aqueous phase *per se* causes a shift in the equilibrium concentrations of Ca and Na in the liquid and solid phases. If the liquid phase is diluted, as by adding distilled water, Ca enters the exchange complex from solution and displaces Na, i.e., by this exchange the relative concentration of Ca is decreased in the aqueous phase and increased in the exchange complex and the bases replaced by Ca accordingly appear in the aqueous phase.

The effect of dilution upon the exchange equilibrium is clearly illustrated by both soils 238 and 239 (table 1 and 2). The absolute as well as the relative amount of Ca of the aqueous phase of both of these soils is decreased in the order of 50 per cent by 27.9- and 30.3-fold dilutions. The principle could be more clearly shown with saline non-calcareous soils, since even in these two soils a part of the Ca replacing Na of the exchange complex was derived from solid  $\text{CaCO}_3$  or  $\text{CaSO}_4$  (note that the Na increase exceeds the  $\text{HCO}_3$  plus  $\text{SO}_4$  increase). In the other soils the effect of dilution upon the absolute amount of calcium in the aqueous phase is largely masked, but as shown in table 4 the

sodium percentages in the aqueous phase of the 1:5 extracts of all soils exceeded the sodium percentages of the displaced soil solutions. It is likewise shown that for each of these soils the sodium percentage of the exchange complex was lower when in equilibrium with 1:5 extracts than when in equilibrium with the soil solution.

If Vanselow's (7) equation G for exchange equilibrium is the correct one, the dilution effect may be mathematically stated for a system containing two active bases and a single active exchange substance. In soils the system is of course a complicated one, since several bases participate and there are present both organic and inorganic materials of complex character that possess base-exchange properties.

$\text{CaCO}_3$  and  $\text{CaSO}_4$  have been emphasized as the important sources of the Ca entering the aqueous phase. It must be recognized, nevertheless, that Ca as well as other bases, including Na, may be derived to a limited extent from other slightly soluble soil constituents.

In the light of the foregoing it becomes apparent that the practice of determining adsorbed sodium and potassium in the soil by subtracting the "water-soluble" Na and K of 1:5 extracts from the total Na and K as found for example in ammonium acetate extracts may result in serious error if the investigator assumes that his results represent the facts as they apply to soils with ordinary field moisture. Values for exchangeable Ca and Mg obtained by subtracting exchangeable Na and K from the total exchange capacity of a soil must also be subject to error if the exchangeable Na and K are not correctly estimated.

In table 3 we have set forth the amounts and percentages of exchangeable bases in the nine soils as ordinarily computed on the basis of Na and K in 1:5 extracts, and also as computed on the basis of the displaced soil solution. Sodium and potassium of the aqueous phase are subtracted from the ammonium-displaced Na and K, and the differences are recorded as replaceable Na and K. The sum of replaceable Na and K is then subtracted from the value for ammonia by aeration and recorded as exchangeable Ca plus Mg. These results show that exchangeable sodium as estimated on the basis of 1:5 extracts may be less to the extent of 50 per cent or more than that estimated on displaced solutions.

It has seemed pertinent to examine these data further to ascertain what relationships might exist between the proportions of bases in the aqueous and absorbed phases. The results of this inquiry are presented in table 4. In this table the sodium percentages of the liquid phases are from table 2; and those of the absorbed phases, from table 3. The corresponding alkali base percentages in the two phases have been calculated by combining sodium and potassium. Total bases of the liquid phase in terms of milligram equivalents per liter are taken from the original work sheets. The latter column, like the total-exchange-capacity column, has been introduced to facilitate comparisons of total bases with the equilibrium ratios presented in the two columns at the

right. Percentage of alkaline earth bases (calcium plus magnesium) is not shown as it is conversely dependent upon percentage of alkali bases.

When the variability in the kind and proportion of mineral and organic substances that may make up the absorbing phase of a soil and the number of cations involved are recognized it is perhaps not surprising that in these diverse soils the ratios between the sodium percentage in the displaced solution and that of the absorbed phase have varied by as much as that represented by the

TABLE 3

*Replaceable cations calculated on basis of displaced soil solutions and on basis of 1:5 extracts*

	MILLIGRAM EQUIVALENTS PER 100 GM. SOIL			Na AS PER CENT TOTAL	Na + K AS PER CENT TOTAL
	Ca + Mg	K	Na		
Soil 238:					
Displaced sol'n.....	19.38	0.67	2.26	10	13
1:5 extract.....	20.53	0.84	0.84	4	8
Soil 239:					
Displaced sol'n.....	14.86	1.02	2.71	15	20
1:5 extract.....	16.68	0.80	1.11	6	10
Soil 2:					
Displaced sol'n.....	7.71	0.53	0.58	7	11
1:5 extract.....	8.04	0.44	0.34	4	9
Soil 4:					
Displaced sol'n.....	6.55	0.89	0.90	11	21
1:5 extract.....	6.76	0.86	0.72	9	19
Soil 4A:					
Displaced sol'n.....	3.53	2.09	2.71	33	58
1:5 extract.....	6.12	2.06	0.15	2	27
Soil 7:					
Displaced sol'n.....	17.04	0.45	1.21	6	9
1:5 extract.....	17.56	0.44	0.70	4	6
Soil 9:					
Displaced sol'n.....	13.00	1.10	0.69	5	12
1:5 extract.....	13.61	1.04	0.14	1	8
Soil 10:					
Displaced sol'n.....	10.57	0.92	3.81	25	31
1:5 extract.....	12.43	0.78	2.09	14	19
Soil 277:					
Displaced sol'n.....	10.78	Tr.	1.96	15	15
1:5 extract.....	11.29	Tr.	1.45	11	11

2.4 to 5.0 range. The corresponding alkali base ratios vary from 1.3 to 3.8. The sodium percentages of the aqueous phase of the soils extracted with five times their weight of water were from 3 to 46 times the corresponding sodium percentages of the absorbed phase. In all cases dilution served to increase the proportion of sodium in the aqueous phase and to decrease the proportion in the absorbed phase. As judged by these data it seems improbable that a mathematical relationship applicable to all soils can be established for the effect of dilution on absorbed base equilibria in complex soil systems.

The percentage of sodium in natural waters ( $\frac{\text{Na} \times 100}{\text{Ca} + \text{Mg} + \text{Na}}$ , concentrations in milligram equivalents) is now recognized by this laboratory as an important characteristic of irrigation water. This recognition results from the observation that when lands are irrigated with waters having high sodium percentages they commonly become deflocculated and impervious. The rapidity with which such effects become apparent is contingent not only upon the total salinity of the water but upon the character of the soil irrigated. It is believed

TABLE 4  
*Ratios of relative concentrations of bases in the aqueous and absorbed phases*

SOIL	LIQUID PHASE			ABSORBED PHASE			Na IN SOL'N Na ABSORBED	AB IN SOL'N AB ABSORBED
	Total bases	Total sodium	Total alkali bases	Total exchange capacity	Total sodium	Total alkali bases		
<i>Displaced soil solutions</i>								
	<i>m.e./liter</i>	<i>per cent</i>	<i>per cent</i>	<i>m.e./100 gm. soil</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
238	334.7	43	50	22.31	10	13	4.3	3.8
239	237.7	39	42	18.59	15	20	2.6	2.1
2	47.6	33	35	8.82	7	11	4.7	3.1
4	27.7	26	29	8.34	11	21	2.4	1.3
4A	3064.6	86	87	8.33	33	58	2.6	1.5
7	57.7	30	30	18.70	6	9	5.0	3.4
9	91.6	18	19	14.79	5	12	3.6	1.6
10	141.9	69	70	15.30	25	31	2.8	2.3
277	56.8	53	53	12.74	15	15	3.5	3.5
<i>1:5 extracts</i>								
238	11.59	64	67	22.31	4	8	16.0	8.4
239	9.35	60	67	18.59	6	10	10.0	6.5
2	2.53	34	43	8.82	4	9	8.5	4.9
4	1.98	27	31	8.34	9	19	3.0	1.6
4A	70.37	92	92	8.33	2	27	46.0	3.5
7	4.09	40	41	18.70	4	6	10.0	6.7
9	4.51	34	37	14.79	1	8	34.0	4.6
10	7.99	79	82	15.30	14	19	5.6	4.4
277	2.29	74	75	12.74	11	11	6.6	6.6

by some, a viewpoint subscribed to by the writers, that this tendency toward deflocculation and impermeability and ultimate unproductiveness is the result of the gradual replacement by sodium of a part of the Ca and Mg of the exchange complex of the soil. Many deflocculated soils are rendered permeable when treated with calcium sulfate. Such observations have supported the base-exchange explanation, but determinations of exchangeable sodium based on 1:5 extracts have generally shown very little sodium in the absorbing complex; sometimes, in fact, an absence of this element is indicated, which is in-

conceivable when substantial concentrations of Na are present in aqueous extracts. Such observations have caused some investigators to doubt the adequacy of the absorbed-sodium interpretation of soil impermeability. The incentive to interrupt other investigations to follow the suggestion afforded by the Chula Vista soils was the possibility that some advancement in the reliability of measuring exchangeable sodium and therefrom a better understanding of the irrigation-water effect might result.

Attention is directed to the data of tables 1 and 2 to illustrate and emphasize an important soil-water relationship; namely, *If we regard solutions displaced from soils as representative of the soil solution, then the significance of more dilute aqueous extracts becomes highly questionable. Only occasionally is it possible to convert the concentrations of constituents found in the dilute aqueous extracts to concentrations as of the soil solution with reasonable accuracy.* The quantity of bicarbonate obtained by aqueous extraction of soils containing carbonate is far greater than that represented in displaced soil solutions. The sulfate obtained by aqueous extraction may exceed that found by displacement; adsorption as well as the limited solubility of calcium sulfate is believed to contribute to this effect. A fair notion of chloride and nitrate concentrations in the soil solution can sometimes be obtained from aqueous extracts, but the bound-water effect may cause the soil solution as presented to the plant to be considerably more concentrated than expected. The proportions and absolute amounts of bases in water extracts are quite different from those of displaced solutions.

Serious manipulative difficulties are admittedly inherent to the present method of displacing the soil solution from different soils. The soil-solution approach to the study of some phases of plant nutrition, salt tolerance, and soil behavior problems as presented under field conditions, however, offers such promise that the displacement procedure becomes deserving of much patient study with a view toward the improvement of its workability as applied to all soils. Recent advances in the development of microanalysis offer promise in this connection, since a material reduction in the quantity of solution required in the laboratory would minimize some of the difficulties.

#### SUMMARY

The proportion and absolute amount of sodium (usually magnesium and potassium also), represented in aqueous extracts of soils are found to be higher than those represented in displaced soil solutions. The proportion (sometimes the absolute amount) of calcium is lower in extracts than in displaced solutions. This release of Na with dilution cannot be ascribed to hydrolysis, and hydrolysis would fail to account for the decrease in Ca. The most satisfactory explanation of this phenomenon is that a cation-exchange reaction takes place when the water-soil ratio is increased. In this exchange, calcium enters the absorbing complex and sodium (sometimes magnesium and potassium) is liberated. New Ca coming into solution from  $\text{CaCO}_3$  and  $\text{CaSO}_4$  with dilution tends to obscure the Ca absorption effect in many soils.



The assumption that Na of aqueous extracts represents Na in the aqueous phase at field moisture appears to be untenable, and accordingly the practice of determining absorbed Na by deducting aqueous-extract Na from ammonium-extract Na may lead to erroneous results. Exchangeable sodium as estimated on the basis of 1:5 extracts may be less than that estimated on displaced solutions to the extent of 50 per cent or more.

The percentage of sodium (as of total bases) in displaced solutions was greater than the percentage of sodium absorbed (corrected on basis of displaced solutions) by 2.4 to 5.0 times. The percentage of sodium of 1:5 extracts exceeded the percentage of sodium absorbed (corrected on basis of 1:5 extracts) by 3 to 46 times.

Bicarbonate as represented by 1:5 extracts of the nine soils was 4 to 17 times greater than that represented by displaced solutions. Sulfate tended to increase with dilution. This increase is ascribed in part to  $\text{CaSO}_4$  coming into solution and in part to  $\text{SO}_4$  adsorption at field moisture. Certain soils gave higher absolute amounts of chloride by displacement than by 1:5 extracts; this is attributed to bound water in the soil, i.e., water not functioning as a chloride solvent and not released during displacement.

#### REFERENCES

- (1) BURD, J. S., AND MARTIN, J. C. 1923 Water displacement of soils and the soil solution. *Jour. Agr. Sci.* (Part 3) 13: 265-295.
- (2) CHAPMAN, H. D., AND KELLEY, W. P. 1930 The determination of the replaceable bases and the base-exchange capacity of soils. *Soil Sci.* 30: 391-406.
- (3) CONRAD, J. P., PROEBSTING, E. L., AND MCKINNON, L. R. 1930 Equipment and procedure for obtaining the displaced soil solution. *Soil Sci.* 29: 323-329.
- (4) GEDROIZ, K. K. 1928 Solonetz soils, their origin, properties, and amelioration. *Nosov Exp. Sta. Bul.* 46.
- (5) HIBBARD, P. L. 1930 Apparatus for percolation at uniform rate and automatic collecting device. *Indus. Engin. Chem. Analyt. Ed.* 2: 404-405.
- (6) KELLEY, W. P., AND BROWN, S. M. 1934 Principles governing the reclamation of alkali soils. *Hilgardia* 8: 149-177.
- (7) VANSELOW, A. P. 1932 Equilibria of the base-exchange reaction of bentonites, permittites, soil colloids, and zeolites. *Soil Sci.* 33.



# ESTIMATION OF REPLACEABLE Na AND K, EXCHANGE CAPACITY, AND DEGREE OF ALKALIZATION IN ALKALI SOILS BY AMMONIUM CARBONATE EXTRACTION

AMAR NATH PURI

*Irrigation Research Institute, Lahore (India)*

Received for publication May 10, 1934<sup>1</sup>

The writer has recently advocated the use of  $\text{Ba}(\text{OH})_2$  for the estimation of exchangeable Na and K in soils (1). The same reagent is employed for finding exchange capacity (2) and degree of alkalization (3) of soils. The use of  $\text{Ba}(\text{OH})_2$  simplifies the estimation to a single titration, and, unlike neutral salt replacement, the preliminary leaching to remove soluble salts is not necessary. Preliminary leaching was, however, required in the case of soils containing alkali sulfates, as these could react with  $\text{Ba}(\text{OH})_2$ , producing NaOH, which introduced a positive error in the estimation. It appeared, however, that ammonium carbonate would be free from this objection. As will be seen from what follows, this reagent proved superior to  $\text{Ba}(\text{OH})_2$  in more than one way for the purpose for which the latter was advocated.

## EXPERIMENTAL

### *Replaceable Na and K by the $\text{Ba}(\text{OH})_2$ method*

This method has already been fully described (1). Briefly it consists in leaching the soil with 1,000 cc. of 0.1 N  $\text{Ba}(\text{OH})_2$ ; passing  $\text{CO}_2$  through the leachate; and evaporating down 500 cc. of the supernatant liquid, followed by extraction of the residue with dilute ammonia when Na and K carbonates are dissolved and estimated by titration after boiling to remove ammonia.

### *Exchange capacity*

The soil is saturated with Na by leaching with NaCl; the exchangeable Na is then determined by leaching with  $\text{Ba}(\text{OH})_2$ .

### *Degree of alkalization*

Degree of alkalization (D.A.) is defined as the percentage of monovalent bases (Na and K) on the total exchange capacity of the soil. The usefulness of D.A. values for characterising alkali soils has already been discussed elsewhere (3).

<sup>1</sup> *Editor's note:* At the author's request, the order of publication of this paper and of one received October 9, 1934 has been reversed.

*Ammonium carbonate method*

Ten to twenty grams of soil are leached with 500 cc. of 0.2  $N$   $(\text{NH}_4)_2\text{CO}_3$  in 100-cc lots. The leachate is evaporated to dryness on a hot plate or in an air oven. The residue is taken up with 50 per cent alcohol and filtered. The filtrate is evaporated to dryness and titrated against standard acid after some water has been added. The titration value gives the amount of exchangeable Na and K in the soil. The titration is more satisfactorily done by adding excess of standard acid and back titrating with standard alkali after boiling the solution to drive away  $\text{CO}_2$  and using brom thymol blue as indicator. For the purpose of the present investigation it was not considered necessary to determine K separately. The exchangeable Na and K are therefore recorded together.

Exchange capacity was measured on the same sample after the  $(\text{NH}_4)_2\text{CO}_3$  treatment by leaching the soil with 500 cc. of  $N$  NaCl or 0.2  $N$  KCl in 100-cc. lots, followed by leaching with 0.2  $N$   $(\text{NH}_4)_2\text{CO}_3$  as described in the foregoing, with the modification that the residue is taken up with a little hot water instead of 50 per cent alcohol and titrated directly after filtration. Degree of alkalization was calculated by the formula

$$\text{D. A.} = \frac{n \ 100}{N}$$

Where  $n$  = m. equivalents of replaceable Na and K and  $N$  = exchange capacity in m. equivalents.

*Comparison with the  $\text{Ba}(\text{OH})_2$  method*

In order to prove the utility of the ammonium carbonate method it was necessary to compare it with the  $\text{Ba}(\text{OH})_2$  method that has already been found to give good results. For this purpose 37 soils were chosen at random from a farm of 600 acres. The idea was to select fields of widely divergent characteristics as regards yield. The results are recorded in table 1. A column giving the yield of rice or barley is also included to show the significance of D.A. values. It is not intended to bring out a strict correlation between D.A. values and yield, because not only were the soils of different series, but the crops were different. Besides, the samples were taken some time after the crop had been harvested when the soil could be expected to have undergone a good deal of change. The general trend of results, however, would serve the purpose of emphasizing the usefulness of characterizing alkali soils on the basis of D.A. values. A much better correlation between the D.A. and yield will be brought out in another series described later.

It will be seen from table 1 that the two methods of finding exchangeable Na and K in soils agree fairly well when the fact that sampling errors must have caused some divergence is considered. The  $(\text{NH}_4)_2\text{CO}_3$  method is simpler and more accurate than the  $\text{Ba}(\text{OH})_2$  method, because, in the former,

TABLE 1

*Comparison of the  $Ba(OH)_2$  and  $(NH_4)_2CO_3$  methods for replaceable Na and K, exchange capacity, and degree of alkalization*

LAB. NO.	EXCHANGEABLE Na AND K		EXCHANGE CAPACITY		DEGREE OF ALKALI-ZATION		YIELD OF RICE OR BARLEY PER ACRE
	Ba(OH) <sub>2</sub> method	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> method	Ba(OH) <sub>2</sub> method	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> method	Ba(OH) <sub>2</sub> method	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> method	
	m.e.	m.e.	m.e.	m.e.	per cent	per cent	lbs.
<b>Rice soils:</b>							
172	4.40	3.55	7.6	7.35	57.9	48.3	205
166	6.70	6.40	8.40	8.30	79.8	77.1	266
168	4.46	3.85	6.64	6.05	67.2	63.6	410
171	5.96	5.70	9.50	9.25	62.7	61.6	451
164	8.70	8.75	9.72	10.50	89.5	83.3	533
162	7.20	6.70	11.30	10.05	63.7	66.7	615
170	3.10	3.90	6.70	6.70	46.3	58.2	656
159	5.90	5.65	7.80	8.50	75.6	66.5	738
167	5.34	4.45	8.40	8.00	63.6	55.6	984
160	8.68	9.00	11.20	10.80	77.5	83.3	1,066
163	8.00	6.80	7.82	8.10	100.0	84.0	1,230
165	4.08	4.55	6.84	7.10	59.6	64.1	1,394
157	6.20	6.50	9.00	8.90	68.9	73.0	1,476
158	3.76	3.00	9.28	7.74	40.5	38.8	1,558
169	2.90	2.90	6.94	6.60	41.8	43.9	1,640
155	5.20	5.20	10.48	8.45	49.6	61.5	1,722
161	5.40	4.80	8.40	8.30	63.7	57.8	1,968
156	7.30	7.75	10.30	9.70	70.9	79.9	2,090
153	2.20	1.95	9.50	8.70	23.6	22.4	2,214
154	1.40	1.00	5.82	5.60	24.1	17.9	2,542
174	2.84	2.40	6.47	6.65	43.9	36.1	2,952
173	2.80	2.40	9.70	8.35	28.8	28.7	3,280
<b>Barley soils:</b>							
179	4.00	3.60	5.40	4.50	74.1	80.0	117
190	2.26	2.10	6.20	6.55	36.4	32.1	122
187	5.70	5.50	10.40	8.90	54.8	61.8	124
188	5.52	6.05	7.70	5.80	71.7	100	161
177	8.40	10.50	10.18	10.60	82.5	99.0	161
176	6.64	5.35	7.80	7.20	85.1	74.3	206
175	4.20	3.95	6.70	7.00	62.7	56.4	283
184	5.18	4.70	7.58	6.70	68.3	70.2	310
185	9.80	8.70	11.20	10.50	87.5	82.8	328
180	5.78	5.95	8.80	8.95	65.7	66.5	431
181	5.72	5.55	9.28	7.00	61.6	79.3	457
178	3.00	2.90	8.80	8.90	34.1	32.6	584
186	1.62	1.65	5.30	4.40	30.6	37.5	638
183	5.60	4.70	7.18	6.25	78.0	75.2	706
182	1.32	0.45	4.42	3.5	29.9	12.9	1,038

the whole of the filtrate is evaporated down and the titration directly gives the total exchangeable Na and K in the soil. Another advantage is that the method can be used in the presence of sulfates, which interfere with the  $\text{Ba(OH)}_2$  method.

For finding exchange capacity the use of NaCl was advocated in a previous paper (2). Subsequent work has shown that KCl is equally good and has the advantage that a 0.2 *N* solution serves the same purpose as a normal solution of NaCl, and, besides, only 500 cc. of the solution is required for completely saturating the soil with K, which is subsequently determined by replacement with  $(\text{NH}_4)_2\text{CO}_3$  just as easily as is Na from the sodium-saturated soil. The values for exchange capacity given in table 1 were obtained by NaCl leaching in one case and KCl in the other. Their general agreement indicates

TABLE 2

*Relation between degree of alkalization  $[(\text{NH}_4)_2\text{CO}_3 \text{ Method}]$  and yield of wheat in Montgomery soils*

SOIL NO.	CULTURAL TREATMENT	n*	N†	D.A.‡	YIELD OF WHEAT GRAIN PER ACRE
		<i>m.e.</i>	<i>m.e.</i>	<i>per cent</i>	<i>lbs.</i>
1	Control I	3.72	5.20	71.5	309
2	Control II	6.38	6.95	91.8	32
3	Flooding and washing I	4.45	5.10	87.3	428
4	Flooding and washing II	4.70	6.75	69.6	69
5	$\text{CaCl}_2$ , 1 ton per acre	2.45	5.30	46.2	627
6	$\text{CaCl}_2$ , 1.5 tons per acre	1.33	5.60	23.7	1004
7	$\text{CaCl}_2$ , 2 tons per acre	1.55	5.95	26.0	1146
8	Gypsum, 1 ton per acre	1.25	5.20	24.0	852
9	Gypsum, 1.5 tons per acre	1.73	6.40	27.0	451
10	Gypsum, 2 tons per acre	2.50	5.60	44.6	766

\* n = Replaceable Na and K.

† N = Exchange capacity.

‡ D.A. = Degree of alkalization.

that either NaCl or KCl can be used, the choice of the latter being a matter of convenience.

The usefulness of D.A. values is brought out in a striking manner in another series of soils from Montgomery District where reclamation experiments were being conducted. These results are given in table 2, which also includes a column showing the cultural treatment received by each plot. It will be seen that the D.A. values generally run according to what one might reasonably expect from the cultural treatment. Determination of D.A. values, therefore, would help in following the course of reclamation in alkali soils.

#### SUMMARY

The use of ammonium carbonate for the estimation of replaceable Na, K, exchange capacity, and degree of alkalization is advocated. The proposed

method is shown to be simpler than the writer's  $\text{Ba}(\text{OH})_2$  method and can be used without subjecting the soil to a preliminary leaching to remove soluble salts.

The usefulness of degree of alkalization determination for characterizing alkali soils is discussed.

#### REFERENCES

- (1) PURI, A. N. 1933 A new method for estimating replaceable Na and K in soils. *Soil Sci.* 36: 355-359.
- (2) PURI, A. N. 1934 A new method of determining base exchange capacity of soils. *Soil Sci.* 37: 105-108.
- (3) PURI, A. N. 1933 Relation between exchangeable sodium and crop yield in Punjab soils and a new method of characterising alkali soils. *Punjab Irrig. Res. Inst. Res. Pub.*, Vol. 4, No. 5.





LIBRARY  
INSTITUTE

## THE LAWS OF SOIL COLLOIDAL BEHAVIOR: XVII. MAGNESIUM SILICATE—ITS BASE-EXCHANGE PROPERTIES<sup>1</sup>

J. S. JOFFE, L. T. KARDOS, AND SANTE MATTSON

*New Jersey Agricultural Experiment Station*

Received for publication September 27, 1934

Very few soil investigations have offered more fundamental data on the make-up of soil and on the intricate problems of soil fertility than the researches on the composition and structure of the soil silicates. The foundation of these researches was laid by Van Bemmelen (2), and these have been followed up throughout the world. In recent years, with the advances made in the realm of colloid chemistry, a closer approach has been made in the study of a number of silicate systems, particularly those of iron and aluminum.

This led to the study of other silicate systems. A number of observed facts on magnesium in plant physiological reactions, on its peculiar mode of movement and translocation in the soil profile, and on its behavior in the exchange complex of the soil, have made the Mg-silicate system of particular interest. A few of these facts, primarily those pertaining to soils, are reviewed before the experimental data on this problem are presented.

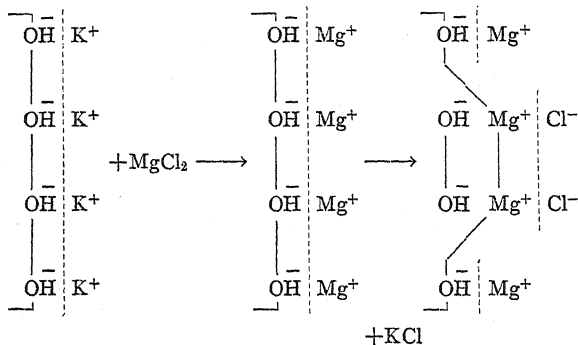
In the case of electrodialytic phenomena, the Mg naturally present in soil colloids acts more like Fe and Al than like Ca or the alkali metals. That is, Mg becomes mobile only after the bulk of the other cations of the strong bases, Ca, K, and Na, have been removed. At the same time Mg is displaceable from a neutral soil by the neutral salt treatment, whereas Fe and Al are not. This phenomenon was described by Oden and Löddesöl (15), Löddesöl (9), and Mattson (11). Kelley, Dore, and Brown (8), investigating the base-exchange properties of bentonites, which are primarily crystalline Mg-aluminum silicates, have shown conclusively that if the natural colloid be sufficiently ground, practically all of the Mg can be made exchangeable. Anderson and Mattson (1) found that the "non-exchangeable" cations present in the natural colloids made up a general average of about two-thirds to three-fourths of the total mono- and divalent bases present. Later Mattson (12), in the light of the work of Kelley, Dore, and Brown, agreed that the cations are non-exchangeable because of their position within the crystal lattice or molecular aggregates. Mattson (13) and Löddesöl (9) both found, however, that if an electrodialyzed soil colloid is saturated by treatment with MgO alone, the Mg is released in a manner similar to the manner of release of the Ca and the alkali metals, but at the same time only about half of the Mg added can be released again by electrodialysis.

Wiegner and Jenny (20) made the important observation that whereas the displacing power of the divalent cations places them in the normal lyotropic order,  $Mg < Ca < Ba$ , the ease with which these cations are displaced when once in combination with the complex is

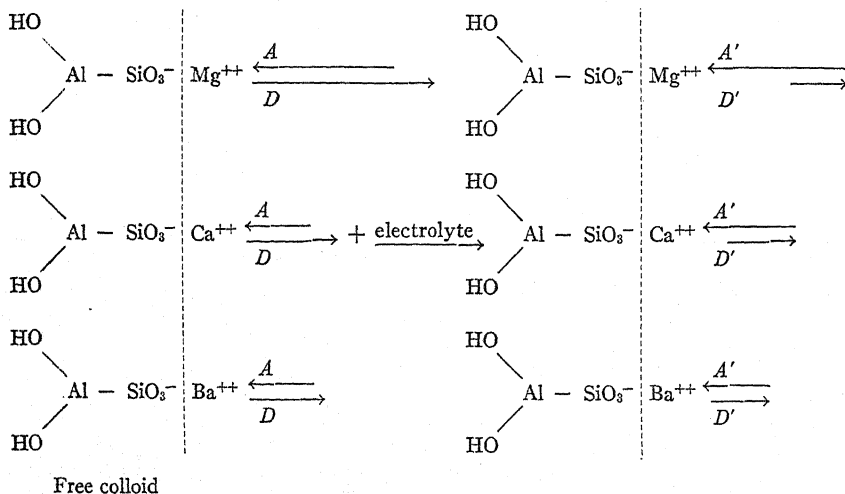
---

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

$\text{Mg} < \text{Ca} < \text{Ba}$ , that is, the Mg is the most difficult to replace as measured against the  $\text{NH}_4$  ion. This condition is anomalous as compared to the lyotropic order and the order of ease of replacement of the alkali cations. Wiegner and Jenny ascribe this phenomenon to the solubility of the hydroxides, which is  $\text{Ba}(\text{OH})_2 > \text{Ca}(\text{OH})_2 > \text{Mg}(\text{OH})_2$ , i.e., the inner layer of anions consists partly of  $\text{OH}^-$  ions which bind the Mg more firmly. Jenny (5) pictures the seat of the exchange in a Helmholtz double layer in which the inner layer consists chiefly of  $\text{OH}^-$ , explaining the "anomalous" behavior of the Mg by the following diagram:



Mattson (13), however, states that Wiegner and Jenny's explanation is insufficient to account for the anomaly, since sesquioxides combine with bases only at pH values above their isoelectric point; however, the introduction of  $\text{SiO}_2$  or other acidoid renders the complex exchange active far over on the acid side of pH 7.0. The bond between cation and complex therefore must be through the silicate group, and the seat of the cation adsorption and exchange is in the free valencies of the silicate anion. Mattson (13) suggests a mechanism which may be diagrammatically represented<sup>2</sup> as follows:



<sup>2</sup> The lengths of the arrows indicate the relative degrees of association and dissociation respectively.

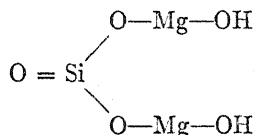
$A$  and  $A'$  = association, a function of the nature of the ions involved.

$D$  = dissociation or critical potential, which is greater the more highly the dissociated diffusible ions are hydrated. In the presence of electrolytes, which suppress the potential or activity of all ions, the potential of the highly multivalent colloidal ion is greatly suppressed, far below its critical value, to  $D'$ . The displaceability will then be governed by the association, for then no electrostatic attraction prevents the slightly hydrated ions from dissociating.

In connection with this anomalous behavior of Mg, we have the observations of soil geneticists concerning the accumulation of Mg in the B horizon of podzols as reported in numerous studies of Rode (18), Gemmerling and Minon (4), and Joffe (6) and the new formation of extremely stable compounds such as the polygorskite, which Poluinov (16) investigated both mineralogically and chemically and found to be composed of a hydrated Mg-aluminum silicate.

MacIntire, Shaw, and Robinson (10) describe the tenaciousness and extent of fixation of Mg in the soil complex when applied as a fertilizer to soils in the form of  $MgCO_3$  and the basic carbonate in excessive amounts. They suggest that the Mg enters directly into the aluminosilicic complex.

In an attempt to contribute some light on the behavior of Mg in silicates, it was decided to start with the simple system  $MgO-SiO_2$ . Numerous studies have been made of  $MgO-SiO_2$  complexes prepared by thermal reactions, i.e., high temperature fusions. However, a search of the literature unearthed very few papers dealing with the preparation of  $MgO-SiO_2$  complexes in the wet way at ordinary temperatures. Jordis (7) stated that by reaction with sodium silicate solutions the alkaline earth hydroxides give metasilicates and at no time orthosilicates. Damiens (3), by mixing  $MgSO_4$  and sodium silicate solutions obtained no definite compound, the composition varying from  $MgO \cdot SiO_2$  to  $MgO \cdot 2SiO_2$ . Vournazos (19) describes the composition of a basic magnesium silicate:



formed by the extended reaction of amorphous silica and MgO at ordinary temperatures in the presence of  $H_2O$ . In none of this work was the pH in the medium considered or controlled.

#### EXPERIMENTAL

The initial series studied was made up by adding 0 to 64 m.e. of Mg, as  $MgCl_2$ , to 19.64 m.e. of  $SiO_2$ , on the basis of  $SiO_3^{2-}$  from  $Na_2SiO_3$ . The series was precipitated in porcelain dishes, adjusted to disappearance of the pink color of phenolphthalein, i.e., approximately pH 8.4, allowed to stand 3 hours, adjusted to pH 8.4 again if the pink color reappeared, placed on the steam bath, and evaporated to dryness. The dried material was taken up with 50 cc. of a normal, neutral (pH 7.0) solution of  $NH_4Cl$ , the mixture was thoroughly disintegrated, allowed to stand 2 hours, and then poured through a dry filter. Twenty-five cubic centimeters of this initial filtrate was analysed for Mg and  $SiO_2$ , and a sample was taken for a pH determination. The complex was then transferred to the funnel and leached with approximately 300 cc. of normal, neutral (pH 7.0) calcium acetate, 20 cc. of  $CaCl_2$ , and then washed free of  $Cl^-$  with  $H_2O$  to insure removal of the excess Ca. The complex was then leached with

neutral (pH 7.0) normal  $\text{NH}_4\text{Cl}$  solution until free of Ca, as determined by  $\text{NH}_4$ -oxalate; approximately 250 cc. of  $\text{NH}_4\text{Cl}$  was used to accomplish this. The residue in the filter was then leached alternately with normal HCl and  $\text{H}_2\text{O}$  until free of Mg. The residue in the funnel was ignited, weighed, treated with HF, and found to consist of  $\text{SiO}_2$  only. The HCl leachate was analyzed for Ca, Mg, and  $\text{SiO}_2$ , but in no case was Ca found. The  $\text{NH}_4\text{Cl}$  leachate was also analyzed for Ca, Mg, and  $\text{SiO}_2$ , after the removal of the  $\text{NH}_4\text{Cl}$  by ignition in platinum dishes. The Ca was determined by titration of its oxalate, and the Mg, as the pyrophosphate. The data are reported in table 138.

The second series was run in quadruplicate, 4 to 32 m.e. of  $\text{MgCl}_2$  being added to 20.03 m.e. of  $\text{SiO}_2$  diluted to 100 cc. in an Erlenmeyer flask. The

TABLE 138  
*Composition and behavior of  $\text{MgCl}_2$  and  $\text{Na}_2\text{SiO}_3$  mixtures*

$\text{Mg}$ AS $\text{MgCl}_2^*$	HCl ADDED	COMPOSITION OF $\text{NH}_4\text{Cl}$ -EXTRACT			EXCHANGEABLE				RESIDUAL		RATIO $\text{SiO}_2/\text{MgO}^\dagger$	
		pH	Mg	$\text{SiO}_2$	$\text{SiO}_2$	Ca	Mg	Total cations	Mg	$\text{SiO}_2$	Initial	Final
m.e.	m.e.		m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.		
0	19.79	4.6	.....	...	0.434	0.084	.....	0.084	.....	18.65	....	....
2	18.05	8.4	0.054	1.3	0.949	0.174	0.699	0.873	0.659	16.98	10.09	25.77
4	16.45	7.6	0.104	0.5	1.237	0.248	1.104	1.352	1.810	15.92	5.04	8.80
8	13.50	7.1	0.690	0.6	1.403	0.461	1.494	1.955	4.203	15.11	2.69	3.59
16	9.97	7.2	3.492	0.5	1.758	0.629	2.146	2.775	6.523	13.98	1.57	2.14
24	7.65	7.1	10.302	...	1.449	0.666	2.534	3.200	8.222	14.78	1.43	1.80
32	6.70	7.1	17.026	...	1.423	0.716	2.662	3.378	8.951	15.34	1.31	1.71
48	4.63	7.3	30.064	...	0.816	0.800	2.098	2.898	10.560	16.27	1.09	1.54
64	3.82	7.3	42.930	...	0.561	0.798	1.818	2.616	11.336	16.83	0.93	1.48

\* 19.635 m.e. of  $\text{SiO}_2$ , as  $\text{Na}_2\text{SiO}_3$ , was added to each mixture.

† Initial = ratio of  $\text{SiO}_2/\text{MgO}$  in complex after 50 cc.  $\text{NH}_4\text{Cl}$  extraction.

Final = ratio of  $\text{SiO}_2/\text{MgO}$  in residual complex, after the exchange action.

pH was adjusted as before to pH 8.4; the volume in every case was made up to 150 cc.; the flasks were stoppered, allowed to stand for 24 hours with intermittent shaking, and then adjusted to pH 8.4 again if the pink color reappeared. The procedure thereafter is essentially the same as in the initial series with the exception that  $\text{H}_2\text{O}$  was used instead of  $\text{NH}_4\text{Cl}$  solution to take up the dried mixture. Also a method of successive exchanges was used, that is, at the end of the first exchange action only one funnel in each group of four was decomposed with  $N$  HCl, the others were subjected to a second exchange action; at the end of the second exchange action two funnels were decomposed, and the remaining funnels, one in each group, subjected to a third exchange action and then decomposition. The results are reported in tables 139 and 140.

## DISCUSSION

From the data in table 138, as well as the data for the quadruplicate series (table 140), we observe that the exchangeable Ca increases steadily as the  $\text{SiO}_2/\text{MgO}$  ratio decreases. What appears to be a contradiction of the results of Mattson (12) and others concerning the relation of the exchange capacity and the  $\text{SiO}_2/\text{R}_2\text{O}_3$  ratios is due to the fact that the true  $\text{SiO}_2/\text{MgO}$  ratios are

TABLE 139  
*The initial composition of the Mg-SiO<sub>2</sub> systems*

Mg ADDED*	NUMBER	HCl	COMPOSITION OF H <sub>2</sub> O-EXTRACT			AVERAGE SiO <sub>2</sub> /MgO IN INITIAL COMPLEX AFTER H <sub>2</sub> O EX- TRACTION (50 cc.)
			pH	Mg	SiO <sub>2</sub>	
<i>m.e.</i>		<i>m.e.</i>		<i>m.e.</i>	<i>m.e.</i>	
4	1	17.32	7.8	0.348	0.126	5.133
	2	17.32	8.0	0.018	0.119	
	3	17.32	8.0	0.072	0.119	
	4	17.32	8.0	0.054	0.126	
8	1	14.08	7.5	1.074	0.113	2.787
	2	14.08	7.5	0.822	0.113	
	3	14.08	7.5	0.786	0.080	
	4	14.08	7.6	0.726	0.086	
16	1	8.81	7.6	3.236	0.073	1.594
	2	8.81	7.5	3.566	0.027	
	3	8.81	7.5	3.516	0.027	
	4	8.81	7.6	3.556	0.040	
24	1	5.57	7.65	8.736	0.033	1.268
	2	5.57	7.65	8.020	0.020	
	3	5.57	7.4	8.194	0.033	
	4	5.57	7.6	8.000	0.027	
32	1	5.57	7.6	15.388	0.013	1.241
	2	5.57	7.6	16.594	0.027	
	3	5.57	7.4	15.862	0.013	
	4	5.57	7.5	15.704	0.013	

\* 20.02 m.e. of SiO<sub>2</sub> was added to each as Na-silicate, in which the ratio of Na<sub>2</sub>O:SiO<sub>2</sub> was 1:1.

obscured by the presence of free silica. The excessively high  $\text{SiO}_2/\text{MgO}$  ratios in the first portion of the series, however, indicate that we do not have a single complex but rather a mixture of the Mg-silicate complex with precipitated silica gel. Therefore, if the minimum  $\text{SiO}_2/\text{MgO}$  ratio (table 140) is assumed to be the composition of the Mg-silicate complex which was formed in each member of the series, it should be possible to calculate the separate ex-

change capacities of the Mg-silicate complex and of the free silica present, by means of a set of simultaneous equations of the form  $Ax + By = C$ , where  
 $A$  = millimoles (mlm.) of MgO-SiO<sub>2</sub> complex calculated from the m.e. of the Mg in the residual mixture (values found in table 141).

$B$  = m.e. of free SiO<sub>2</sub> calculated from the difference of SiO<sub>2</sub> in MgO-SiO<sub>2</sub> complex and the total SiO<sub>2</sub> in the residual mixture (values found in table 141).

$x$  = m.e. of exchangeable Ca per mlm. of the MgO-SiO<sub>2</sub> complex.

TABLE 140  
*The exchangeable ions in Mg-silicate complex*

	EXCHANGEABLE Ca	DISPLACEABLE Mg	DISPLACEABLE SiO <sub>2</sub>	SiO <sub>2</sub> /MgO RATIO AT END OF EXCHANGE†
<i>1st exchange (average of four funnels)</i>				
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	
4*	0.226	1.004	0.903	7.692
8	0.388	1.294	1.059†	3.610
16	0.744	1.559	0.922	1.862
24	0.933	1.950	1.001	1.565
32	0.985	1.994	0.982	1.548
<i>2nd exchange (average of three funnels)</i>				
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	
4	0.153	0.531	0.689	14.272
8	0.293	0.940	0.918	4.695
16	0.677	1.113	0.921	1.946
24	0.726	1.176	0.851	1.747
32	0.785	1.202	0.939	1.711
<i>3rd exchange</i>				
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	
4	0.096	0.256	0.498	30.030
8	0.219	0.571	0.670	5.917
16	0.479	0.875	0.823	2.037
24	0.608	0.920	0.852	1.751
32	0.598	1.047	0.925	1.730

\* Numbers correspond to the systems indicated in first column, table 139.

† Average of two funnels.

‡ These do not represent the true SiO<sub>2</sub>/MgO ratios, for there is free SiO<sub>2</sub> present.

$y$  = m.e. of exchangeable Ca per m.e. of the free SiO<sub>2</sub>.

$C$  = total m.e. of exchangeable Ca (values in table 140).

A typical example of the application of the method of simultaneous equations to the data obtained during the first exchange action follows:

Using the pairs of values for the 8 and 16 m.e. series from table 141 and the corresponding values of the exchangeable Ca for the first exchange action from table 140 we have:

$$2.313x + 9.487y = 0.388 \quad (A)$$

$$4.635x + 2.764y = 0.744 \quad (B)$$

TABLE 141  
The relation of the exchange capacities to the true\*  $\text{SiO}_2/\text{MgO}$  ratios

The relation of the exchange capacities to the composition																																															
1st exchange Compn. of complex assumed for nos. 4, 8, 16, 24 = (SiO <sub>2</sub> ) <sub>1.24</sub> · MgO Compn. of complex assumed for no. 32 = (SiO <sub>2</sub> ) <sub>1.48</sub> · MgO																																															
Series number†	4					8					16					24					32																										
m.e. Mg } present‡ m.e. SiO <sub>2</sub> } mlm. of Mg complex§ m.e. free SiO <sub>2</sub>	2.252					4.626					9.271					11.735					12.055																										
	17.273					16.726					17.273					18.638					18.67																										
	1.126					2.313					4.635					5.867					6.027																										
	13.749					9.487					2.764																																				
Series number																Series number																Series number															
4																4																4															
A																A																A															
B																B																B															
x**																x																x															
y																y																y															
0.152																0.1503																0.189															
0.170																0.1503																0.187															
0.160																3.570																2.735															
0.159																4.359																3.649															
0.163																4.314																3.574															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167																0.182																0.167															
0.167</																																															

\* After correcting for the free  $\text{SiO}_2$ .

† Nos. 4, 8, 16, 24, and 32 indicate m.e. of Mg added in making up the complex.

‡ As found by analyzing the residual complex after the exchange action.

§ Calculated on the basis of the m.e. of Mg in the complex, designated as A in the lower tables.

|| Difference (designated as B in the lower tables) between the total m.e. of  $\text{SiO}_2$  present and the m.e. of  $\text{SiO}_2$  combined with Mg, the latter  $\text{SiO}_2$  being = to the product of the "true"  $\text{SiO}_2/\text{MgO}$  ratio assumed and the m.e. of Mg complex present.

\*\* x and y—the exchange capacities in m.e. per mlm. of Mg-complex and per m.e. of free  $\text{SiO}_2$  respectively as calculated from the linear equations.

Solving these equations simultaneously for  $y$ , we get:

$$10.721x + 43.972y = 1.798$$

$$10.721x + 6.393y = 1.721$$

$$37.579y = 0.077$$

$$y = 0.0020 \text{ m.e.}$$

Substituting this value of  $y$  in equation (A) we get  $x = 0.160$  m.e.

The values of  $x$  for the last two members of each series was obtained by dividing the m.e. of exchangeable Ca by the millimoles of the complex present, since free silica was assumed to be absent. Thus for series 24 during the first exchange we have:

$$x = \frac{0.933}{5.867} = 0.159 \text{ m.e.}$$

TABLE 142  
*Loss of the complex during exchange procedure*

Mg ADDED*	LOSS OF MgO			LOSS OF SiO <sub>2</sub>			RATIO SiO <sub>2</sub> : MgO lost lost		
	I†	II	III	I	II	III	I	II	III
m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.			
4	1.625	1.187	0.663	2.624	2.200	3.000	1.615	1.853	4.525
8	2.522	1.619	1.103	3.193	2.639	2.791	1.266	1.630	2.530
16	3.260	2.130	1.671	2.705	3.393	2.746	0.830	1.593	1.643
24	4.027	3.017	1.419	1.624	3.148	2.447	0.403	1.043	1.724
32	4.058	3.427	1.480	1.333	3.905	2.401	0.328	1.139	1.622

\* 20.02 m.e. SiO<sub>2</sub> added to each mixture (m.e. on basis of SiO<sub>3</sub><sup>2-</sup>).

† I, II, and III indicate the respective data during the first, second, and third exchange actions.

At the same time one can now readily see in the data thus tabulated in table 141 the trend of the values of  $x$  to increase as the true SiO<sub>2</sub>/MgO ratios increase, i.e., after correcting for the free SiO<sub>2</sub>. From the data in table 141 it is apparent that during the first exchange, with a complex having a SiO<sub>2</sub>/MgO ratio of 1.565, there is an average exchange capacity of 0.161 m.e. (average value of  $x$ ) per millimol of the complex, whereas during the second exchange, with a complex having a SiO<sub>2</sub>/MgO ratio of 1.747, there is an average exchange capacity of 0.180 m.e. per millimol of the Mg complex.

The agreement in the values of  $x$  and  $y$  is very good, and it is significant that the calculated exchange capacity of the free silica is of the same order of magnitude as the value of 0.0048 m.e. per m.e. of SiO<sub>2</sub> obtained directly, from the data in table 138, from the sample to which no magnesium was added.

Inasmuch as the exchange capacity of the silica is low, the linear nature of the foregoing equation should become evident by plotting the exchangeable Ca



against the mlm. of the Mg-silicate complex present. Figure 40 shows a strikingly close adherence to the linearity of the function.

A similar analysis, i.e., application of the method of simultaneous equations with base-exchange data correlated with pH measurements, should enable one

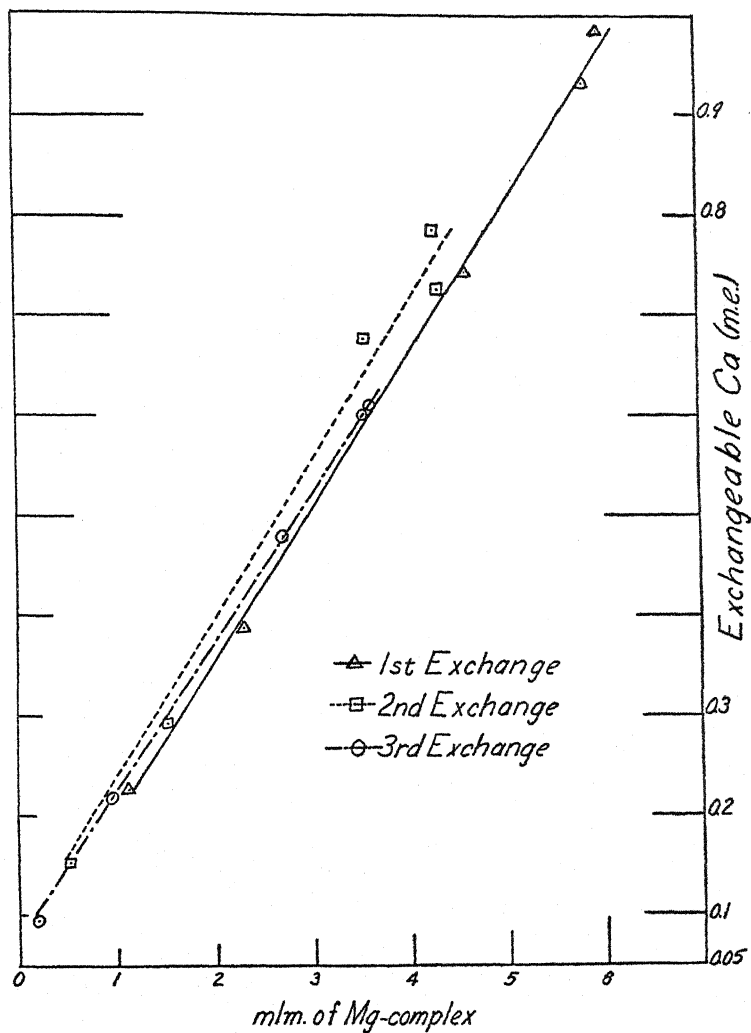


FIG. 40. THE LINEAR RELATIONSHIP BETWEEN THE EXCHANGEABLE Ca AND THE MILLIMOLS OF Mg-SILICATE COMPLEX PRESENT

to distinguish the supposedly different ferric silicates obtained by Ray and Ganguly (17) in their studies of Na-silicate solutions.

The presence of the Mg and the  $\text{SiO}_2$  in the exchange leachate indicates that appreciable hydrolysis of the complex had taken place. In order to approxi-

mate the relative ease of hydrolysis of the complex in each group, the ratio of the total Mg lost during the exchange action to the arithmetical mean of the Mg present at the beginning and at the end of the exchange action was calculated. The ratios (table 143) indicate that the free silica present in the lower members of the series apparently has a mobilizing action upon the Mg. A similar mobilizing action was observed by Mattson and Hester (14) in the Al-SiO<sub>2</sub> system. The loss of Mg in such relatively excessive amounts during the leaching procedures is undoubtedly in great measure due to the fact that the pH of the leaching agents was 7.0, whereas the compound precipitated was the form stable at pH 8.4. Therefore, an acid hydrolysis would result during the leaching, which should result in a continuous reversion toward the form of the complex more stable at pH 7.0. Precisely this is indicated by the SiO<sub>2</sub>/MgO ratios (table 140) of the 24 and 32 m.e. systems, as well as by the hydrolytic ratios of the same two systems (table 143).

TABLE 143  
 "Hydrolytic" ratios\*

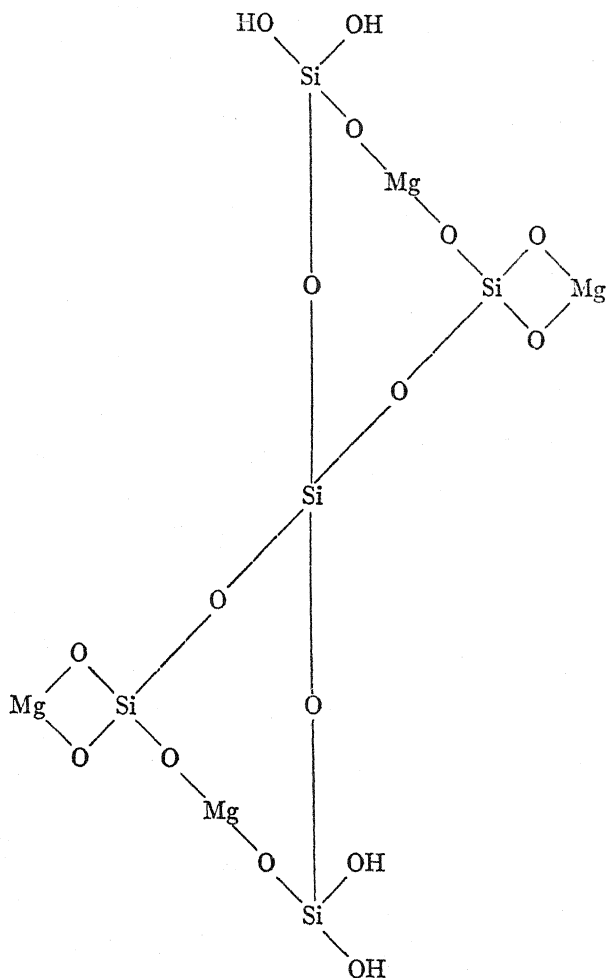
SERIES NUMBER	I†	II	III
4	0.530	0.716	0.905
8	0.428	0.424	0.449
16	0.299	0.260	0.265
24	0.293	0.295	0.177
32	0.288	0.331	0.188

\* Ratio of m.e. of Mg lost during the exchange action to the arithmetical mean of the Mg present at the beginning and at the end of the exchange action.

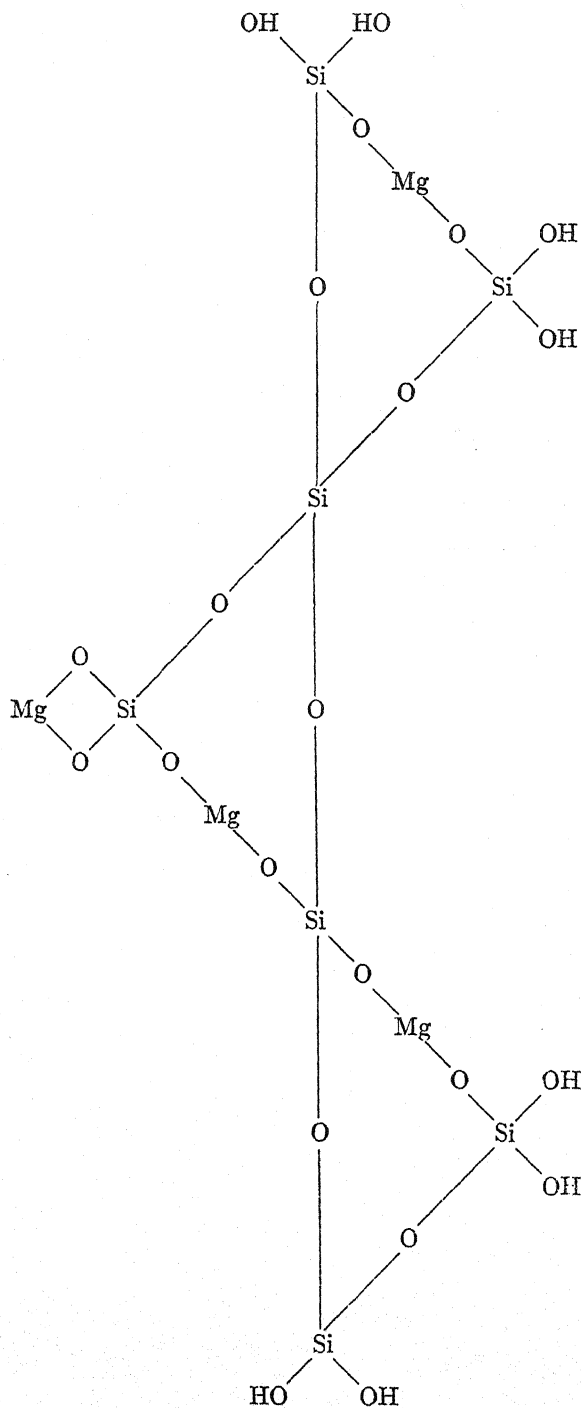
† I, II, and III indicate the respective data during the first, second, and third exchange actions.

MacIntire, Shaw, and Robinson (10), in a somewhat similar manner, explain the continued exchange of Mg and the concomitant disruption of the alumino-silicic acid complex during the determination of the exchangeable bases of soil which was previously treated with excessive amounts of MgCO<sub>3</sub> and Mg basic carbonates.

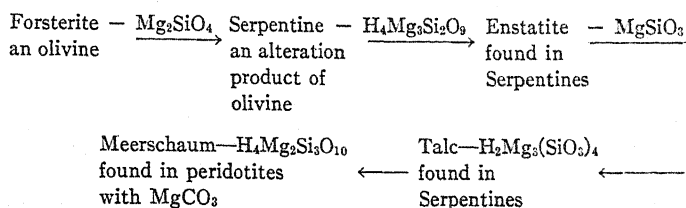
It is evident from the data in tables 139 and 140 that the compound formed by the interaction of MgCl<sub>2</sub> and Na<sub>2</sub>SiO<sub>3</sub> at pH 8.4 is not stoichiometrically of the form known as the metasilicate, i.e., MgSiO<sub>3</sub>. The composition indicates, rather, a higher silica content, a SiO<sub>2</sub>/MgO ratio of 1.25, which might be pictured as follows, indicating the locking of the Mg within the complex:



As the complex was leached with a reagent at pH 7.0, according to the principles of isoelectric weathering we should obtain a compound of higher  $\text{SiO}_2/\text{MgO}$  ratio. The compound present after three successive exchange actions, having a  $\text{SiO}_2/\text{MgO}$  ratio of 1.75, could be represented as follows:



In the 24 and 32 m.e. samples a comparison of the ratios  $\text{SiO}_2$  lost/ $\text{MgO}$  lost (table 142) during the exchange procedure with the  $\text{SiO}_2$ / $\text{MgO}$  ratios of the residual complex (table 140) indicates a sort of isoelectric hydrolysis which finds a singularly similar counterpart in the  $\text{MgO-SiO}_2$  minerals found in nature, e.g., we have the series of minerals:



each one of which could be derived from the preceding mineral by a process of isoelectric weathering involving acid hydrolysis. It would be extremely interesting to investigate the association of these various minerals with each other from this viewpoint.

#### SUMMARY

The theories concerning the "anomalous" behavior of Mg in electrodialysis and base-exchange phenomena are discussed.

The procedure employed permitted a study of the isoelectric hydrolysis of Mg-silicate mixtures together with base exchange determinations.

Mixtures containing free silica, together with the Mg-silicate complex, yielded to a mathematical interpretation whereby the individual exchange capacities of the free silica and the Mg-silicate complexes could be determined.

It is pointed out that the mechanism of isoelectric hydrolysis is capable of accounting for various Mg-silicate minerals found in natural deposits.

Several formulas are suggested to illustrate the composition of the Mg-silicate complex at pH 8.4 and pH 7.0.

#### REFERENCES

- (1) ANDERSON, M. S., AND MATTSON, SANTE 1926 Properties of the colloidal soil materials. U. S. Dept. Agr. Bul. 1452.
- (2) BEMMELEN, VAN, J. M. 1910 Die Absorption. Ges. Abhandl., Dresden.
- (3) DAMIENS, A. 1925 An artificial magnesium silicate. *Compt. Rend. Acad. Sci. [Paris]* 180: 1843-1845.
- (4) GEMMERLING, V. V., AND MONIN, S. A. 1930 Description of soil samples gathered along the route of the excursion of the Second International Congress of Soil Science (English). Organ. Com. 2nd Internatl. Cong. Soil Sci., Moscow.
- (5) JENNY, HANS. 1926 Cation and anion exchange on the interfaces of permutites. *Kolloid chem. Beihefte* 23: 428-472.
- (6) JOFFE, J. S. 1933 Lysimeter studies: II. The movement and translocation of soil constituents in the soil profile. *Soil Sci.* 35: 239-57.
- (7) JORDIS, E. 1906 Precipitation of alkaline earth silicates. *Ztschr. Angew. Chem.* 19: 1697-1708.

- (8) KELLEY, W. P., DORE, W. H., AND BROWN, S. M. 1931 The nature of the base exchange material of bentonites, soils and zeolites, as revealed by chemical investigation and X-ray analysis. *Soil Sci.* 31: 25-55.
- (9) LÖDDESÖL, AASULV 1932 Investigations concerning separation of similarly charged ions from soils by electrodialysis. *Soil Sci.* 33: 375-394.
- (10) MACINTIRE, W. H., SHAW, W. M., AND ROBINSON, B. 1934 The distinction between Mg absorbed and that exchangeable, four years after lysimeter incorporations of oxides and carbonates. *Soil Sci.* 38: 289-303.
- (11) MATTSON, SANTE 1926 Electrodialysis of the colloidal soil material and the exchangeable bases. *Jour. Agr. Res.* 33: 552-67.
- (12) MATTSON, SANTE 1931 The laws of soil colloidal behavior: V. Ion adsorption and exchange. *Soil Sci.* 31: 311-331.
- (13) MATTSON, SANTE 1933 The laws of soil colloidal behavior: XI. Electrodialysis in relation to soil processes. *Soil Sci.* 36: 149-163.
- (14) MATTSON, SANTE, AND HESTER, J. B. 1933 The laws of soil colloidal behavior: XII. The amphoteric nature of soils in relation to aluminum toxicity. *Soil Sci.* 36: 229-244.
- (15) ODEN, SVEN, AND LÖDDESÖL, A. 1930 The relation between the degree of base saturation and the hydrogen ion concentration for some soils. Meddel. 392 Centralanst. Avdel för Lantbruksskemi. 40.
- (16) POLUINOV, B. 1915 Secondary minerals in ortstein horizons. *Dokuchaev Soil Inst.* 2: 125-138 (Russian). (Translated by J. S. Joffe.)
- (17) RAY, R. C., AND GANGULY, P. B. 1930-31 The optimum conditions for the formation of silica gel from alkali silicate solutions I, II. *Jour. Phys. Chem.* 34: 35: —.
- (18) RODE, A. A. 1930 An excursion to the Lisino experimental forest of the Leningrad Technical Academy of Forestry. Second International Congress of Soil Science, Moscow (English). Acad. Sci. U. S. S. R.
- (19) VOURNAZOS, A. CH. 1931 Hydraulic and white Mg cement. *Ztschr. Anorgan. u. allg. Chem.* 200: 237-244.
- (20) WIEGNER, G., AND JENNY, H. 1927 On basic exchange. *Abs. Comm. II, 1st Internatl. Cong. Soil Sci.*, pp. 46-51.

# MATHEMATICAL RELATIONS BETWEEN TOTAL EXCHANGE CAPACITY AND ABSORPTION OF AMMONIUM AND POTASSIUM BY SOILS

J. F. FUDGE

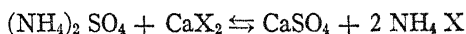
*Texas Agricultural Experiment Station*

Received for publication November 19, 1934

The absorption by soils of bases from salt solutions has been the subject of a great deal of study since its discovery by Way in 1849. Recently, since the clarification of ideas concerning total exchange capacity and the exchange complex, several mathematical equations have been proposed to express the relation between the total exchange capacity and the absorption of bases. The present paper gives the results of a study conducted in an effort to determine which of these various equations expresses most accurately the relation between the base exchange complex and the quantities of ammonium or potassium absorbed by soils from dilute solutions of ammonium or potassium sulfate.

## EQUATIONS CONSIDERED

According to the law of mass action, the reaction between a solution of ammonium sulfate and a base exchange complex saturated with calcium can be represented by the following equation:



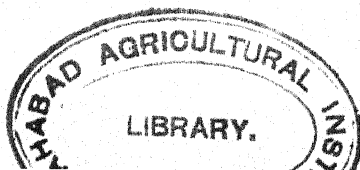
Kerr (2) applied the law of mass action to the equilibrium conditions. He assumed the active masses of the bases in the exchange complex to be proportional to their total concentrations and the ionic concentrations of ammonium and calcium as present only in the liquid phase. The equation thus developed is as follows at equilibrium:

$$\frac{(\text{NH}_4^+)^2 (\text{CaX}_2)}{(\text{Ca}^{++}) (\text{NH}_4\text{X})^2} = K \quad (A)$$

The quantities within the parentheses are active concentrations. It is assumed that the exchange complex acts as though it were in solution.  $K$  is a constant.

Vanselow (5) has suggested that instead of acting as though in solution, the base exchange compounds form a series of mixed crystals. This theory introduces another factor so that equation (A) becomes as follows:

$$\frac{(\text{NH}_4^+)^2 (\text{CaX}_2) (\text{CaX}_2 + \text{NH}_4\text{X})}{(\text{Ca}^{++}) (\text{NH}_4\text{X})^2} = K \quad (B)$$



Csiky (1) quotes Vageler and Waltersdorf (4) as stating that the relation between the amounts of exchanged ions and the quantity of replacing reagent used is a very regular adsorption curve. They suggest that this curve is a hyperbola corresponding to the hyperboloid form of the dissociation residue curve, and can be characterized by the asymptote formula of the hyperbola as follows:

$$y = \frac{x \cdot S}{x + C} \quad (C)$$

In this equation,  $x$  is the quantity of salt used,  $y$  is the quantity absorbed,  $S$  is the limiting value of the adsorption capacity, and  $C$  is the half value of the limiting value.

Patten and Waggaman (3) in 1908, stated that the absorption of potassium is closely represented by the formula

$$\frac{dy}{dv} = (A - y)$$

in which  $y$  is the amount absorbed from  $v$  cc. of solution and  $A$  is the value at the limit of adsorption. If the volume be kept constant, the concentration,  $x$ , may be introduced into the equation to give the following:

$$\frac{dy}{dx} = K(A - y) \quad (D)$$

G. Wiegner (6) states that the relation between the quantity of an ion in solution and the quantity taken up by the soil is represented by the equation

$$y = KC^{1/p} \quad (E)$$

in which  $y$  represents the quantity taken up by the soil,  $C$  represents the quantity in solution at equilibrium, and  $K$  and  $p$  are constants determined experimentally.

The plan of the present work was to determine the quantities of ammonium and potassium absorbed by soils varying in total exchange capacity from ammonium or potassium sulfate solutions of various concentrations, and then to use these data to test different equations already given and ascertain which most closely represented the actual process of absorption.

#### ABSORPTION OF AMMONIUM AND POTASSIUM

Absorption of ammonium or potassium was determined in one series, using 50 gm. of soil and 200 cc. of water containing the desired quantity of ammonium sulfate or potassium sulfate. The mixture was shaken 1 hour in an end-over-end shaking machine; preliminary experiments showed that this gave the same results as occasional shaking during 24 hours. The soil was then filtered off; ammonia was determined in the filtrate by distillation into standard hydro-



chloric acid; and potassium, by the chloroplatinate method. The solutions used contained the equivalent of 2, 4, 8, and 16 m.e. of ammonium sulfate or of 0.85, 4, and 8 m.e. of potassium sulfate per 100 gm. of soil.

The quantities of ammonium and potassium absorbed by a number of soils are given in table 1. In general, the base absorbed varied with the exchange capacity, but the relation is only approximate. The soils absorbed a little more potassium than ammonium, the average difference being 11 per cent in

TABLE 1

*Ammonium absorbed from ammonium sulfate and potassium absorbed from potassium sulfate solutions of various concentrations*

LABORATORY NUMBER	SOIL TYPE	TOTAL EXCHANGE CAPACITY OF SOIL	AMMONIUM SULFATE IN ORIGINAL SOLUTION				POTASSIUM SULFATE IN ORIGINAL SOLUTION		
			2	4	8	16	0.85	4	8
			m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
12595	Norfolk fine sand	1.46	0.06	0.22	0.72	0.86			
12592	Norfolk fine sandy loam	2.62	0.33	0.68	1.03	1.44			
20725	Hockley fine sandy loam	3.00	0.41	0.77	1.31	1.55	0.36	0.91	1.66
12597	Susquehanna fine sandy loam	3.08	0.31	0.65	1.06	1.20	0.31	0.69	1.10
18230	Kirvin fine sandy loam	4.98	0.53	1.13	2.20	4.18			
12596	Susquehanna fine sandy loam	6.00	0.24	0.70	1.37	1.83	0.23	0.88	1.63
12647	Miller fine sandy loam	6.44	0.79	1.52	2.24	3.22			
12652	Yohola silt loam	11.30	0.91	1.73	3.04	4.65			
12518	Crockett loam	13.71	0.49	1.26	2.66	4.32	0.42	1.63	3.12
12651	Yohola silt loam	16.08	0.89	1.78	3.69	5.88			
9348	Unknown	18.31	1.18	2.30	4.19	6.80	0.67	2.46	4.51
12519	Crockett loam	18.49	0.93	1.88	3.52	5.47			
12642	Trinity fine sandy loam	18.70	0.60	1.94	3.78	5.53			
20721	Victoria clay loam	21.28	1.41	2.38	3.96	7.22			
12659	Wilson clay loam	23.43	0.97	2.18	4.03	6.66	0.54	2.39	4.06
12677	Lufkin clay loam	27.45	1.15	2.30	4.42	7.36	0.53	2.38	4.22
12581	Trinity clay	27.60	1.44	2.54	4.70	8.11	0.64	2.74	5.53
12580	Trinity clay	29.60	1.27	2.53	4.73	8.31	0.63	3.06	5.11
12533	Wilson clay loam	37.24	0.97	2.65	5.32	9.34	0.62	3.10	5.73
7147	Unknown	44.04	1.08	2.82	5.41	9.55	0.64	3.06	5.97
12571	Houston stony clay	44.13	1.17	2.73	4.73	8.28			
21067	Trinity clay	45.81	1.45	3.03	5.66	10.19	0.70	3.05	6.06
18226	Houston black clay	47.12	1.50	2.82	5.58	9.87			

the case of the 4 m.e. solution and 12 per cent with the 8 m.e. solution. It is seen from table 1 that soils of widely varying total exchange capacity absorbed similar quantities of bases; soils of similar exchange capacity absorbed different quantities of bases. The differences in absorption may be due partly to capillary adsorption and not entirely to base exchange. They suggest, however, that in the different soils, the exchange complexes are significantly different with respect to their activity of reaction with bases in the soil solution. If this

be true, it is obvious that the values of the constants in the various equations would vary significantly in different soils, and any average value would be only approximate.

In order to ascertain more definitely whether or not differences in absorption were caused by differences in the nature as well as the quantity of the exchange complex, a second series of absorption tests was made, in which a constant amount of exchange capacity was used. A quantity of each soil containing 10 m.e. exchange capacity was used with 2.5 and with 20.0 m.e. ammonium sulfate in 500 cc. of water.

The results are given in table 2. The quantity of ammonium absorbed from 2.5 me. of ammonium sulfate by 10 m.e. exchange complex varied in the different soils from 0.78 m.e. to 1.06 m.e. From 20.0 m.e. of ammonium sulfate, the quantities absorbed varied from 3.64 m.e. to 5.04 m.e. The results show significant differences in absorption, which may be due to differences in the nature of the exchange complexes of the various soils.

TABLE 2

*Absorption of ammonium by quantities of soil containing 10 m.e. of exchange complex*

LABORATORY NUMBER	TOTAL EXCHANGE CAPACITY OF SOIL	WEIGHT OF SOIL USED	AMMONIUM SULFATE IN ORIGINAL SOLUTION			
			2.5 m.e.		20.0 m.e.	
			m.e.	per cent	m.e.	per cent
20725	3.00	333	1.04	41.7	4.16	20.8
18230	4.98	201	1.01	40.3	4.86	24.3
12651	16.08	62.2	0.94	37.3	4.25	21.2
12642	18.70	53.4	0.78	31.0	3.64	18.2
20721	21.28	47.0	1.05	42.0	4.70	23.5
12580	29.60	33.8	1.03	41.5	4.65	23.2
12533	37.24	26.9	1.06	42.4	5.04	25.2
21067	45.81	21.8	1.04	41.7	4.68	23.4

#### RELATION OF RESULTS TO THE VARIOUS MATHEMATICAL EQUATIONS

The data presented in table 1 were used to calculate values in the various mathematical equations previously mentioned. The quantity of ammonium or potassium absorbed was taken to be equal to the quantity of ammonium or potassium complex formed and equal to the quantity of calcium ion in solution at equilibrium. The quantity of calcium complex was assumed to be the total exchange capacity minus the ammonium or potassium complex produced in the absorption. These assumptions are not strictly correct, but the divergences are of relatively very small importance. The various equations are discussed in the following sections.

#### *Mass law equation of Kerr*

Values of  $K$  were calculated for the equation proposed by Kerr (2),

$$\frac{(\text{NH}_4^+)^2 (\text{CaX}_2)}{(\text{Ca}^{++}) (\text{NH}_4\text{X})^2} = K \quad (A)$$

The results are given in table 3. It must be remembered that the values were calculated on the basis that the entire original exchange complex was taken up by calcium. However, small quantities of cations of a different valence were undoubtedly present and had some slight effect on the results obtained. The value of  $K$  is seen to vary widely from soil to soil, and also in the same soil with different quantities of ammonium or potassium. For many of the soils the values of  $K$  decrease with an increase in the concentration of the solution. In

TABLE 3

Calculated values of  $K$  in the equation,  $\frac{(NH_4^+)^2 (CaX_2)}{(Ca^{++}) \times (NH_4X)^2} = K$

LABORATORY NUMBER	TOTAL EXCHANGE CAPACITY OF SOIL	AMMONIUM SULFATE IN ORIGINAL SOLUTION				POTASSIUM SULFATE IN ORIGINAL SOLUTION		
		2 m.e.	4 m.e.	8 m.e.	16 m.e.	0.85 m.e.	4 m.e.	8 m.e.
	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
12595	1.46	24,370.	1,664.0	105.6	186.0			
12592	2.62	178.7	68.0	70.7	83.3			
20725	3.00	95.0	52.2	33.7	81.3	14.1	26.5	14.8
12597	3.08	271.7	99.3	81.7	300.0	27.1	79.7	70.8
18230	4.98	64.6	41.8	8.8	1.5			
12596	6.00	1,261.0	168.2	79.2	136.6	229.5	73.2	38.5
12647	6.44	16.8	8.6	12.4	15.7			
12652	11.30	16.4	9.6	7.2	8.6			
12518	13.71	256.2	50.2	16.7	14.1	33.2	15.7	8.3
12651	16.08	27.3	12.5	4.6	5.2			
9348	18.31	7.0	3.8	2.7	3.1	1.9	2.8	1.8
12519	18.49	25.0	11.2	6.9	8.8			
12642	18.70	164.9	9.7	7.5	8.5			
20721	21.28	2.5	3.8	4.6	3.0			
12659	23.43	26.1	6.8	4.7	5.0	14.0	5.0	4.5
12677	27.45	12.5	6.0	3.4	3.8	18.5	4.9	4.4
12581	27.60	2.8	3.3	2.4	1.8	4.6	2.0	0.8
12580	29.60	7.4	3.5	2.5	2.1	5.6	0.8	1.5
12533	37.24	42.2	3.4	1.5	1.3	8.1	0.9	0.9
18546	38.10	9.6	2.8	1.7	1.7			
7147	44.04	28.9	2.6	3.1	1.7	7.3	1.2	0.7
12571	44.13	18.5	3.3	3.9	3.8			
21067	45.81	4.4	1.5	1.2	1.1	3.0	1.4	0.7
18226	47.12	3.4	2.8	1.4	1.5			

some soils, this decrease is comparatively small, while in others, it is very great. With a given solution, the value of  $K$  in general decreases with the increase in total exchange capacity of the different soils, but the decrease is by no means regular. The quantities of bases absorbed by soils of low exchange capacity from solutions of low concentrations are usually much too small to give satisfactory agreement with values of  $K$  calculated from solutions of higher concentrations. It is possible that under these conditions capillary absorption of the cations may be of such relative importance as to overbalance the effect of

the exchange complex. The values of  $K$  for the different soils and solutions are much greater and much more variable under the conditions previously named than with soils of high exchange capacity and more concentrated solutions.

The values of  $K$  for the absorption of potassium do not vary as much as the corresponding values for the absorption of ammonium but these, too, are very variable. They are as a rule much lower than the corresponding values for ammonium. The average increases in quantity of potassium absorbed, as compared to ammonium absorbed, were 11 per cent and 12 per cent for the 4 m.e. and 8 m.e. solutions, respectively, while the corresponding decreases in values of  $K$  were 43.7 per cent and 39.0 per cent. This shows that comparatively small differences in the quantity of base absorbed may produce large differences in values of  $K$ .

When constant amounts of exchange capacity were used (see the data in table 2), the values of  $K$  for six of the eight soils were nearly the same, averaging 17.2 for the 2.5 m.e. solution and 12.4 for the 20.0 m.e. solution. Values of  $K$  for Nos. 12651 and 12642, respectively, were 26.5 and 57.5 for the 2.5 m.e. and 19.4 and 35.3 for the 20.0 m.e. solutions. For a decrease of 25.7 per cent in ammonium absorbed from the 2.5 m.e. solution, the value of  $K$  for No. 12642 increased 334.3 per cent. This also shows the marked influence of small differences in quantity of base absorbed upon the value of  $K$ .

Kerr (2) reports results with a Hawaiian soil having a total exchange capacity of 14.77 m.e. per 100 gm. of soil. The quantities of ammonium chloride in the solutions used varied from 6.24 m.e. to 21.55 m.e., thus being considerably greater than those used in this work. For the several solutions which Kerr used, the values of  $K$  were between 12.5 and 13.3. This value is somewhat higher than that for five of the six soils in table 3 varying from 10 m.e. to 20 m.e. exchange capacity. No. 12518, a Crockett loam, gave much higher values than those of Kerr. Vanselow (5) worked with the extracted colloids of one soil and 0.1  $N$  solution, and calculated his results to 100 gm. of colloid; the exchange capacity and the salt concentrations were equivalent to 67.5 m.e. throughout. He obtained a value of  $K$  in equation (A) of about 2.20. This value is in fair agreement with the results with ammonium reported in table 3 for the eight soils of exchange capacity over 27.5 m.e. and solutions of 8 to 16 m.e., but corresponding values for potassium are appreciably lower. The values of  $K$  obtained by equation (A) vary markedly in some soils with a variation in concentration of solution, vary widely between different soils with the same concentration of solution, and are subject to great variation with small differences in quantities of base absorbed. Consequently, equation (A) does not seem to be a good expression of the conditions involved.

#### *Mixed crystal equation of Vanselow*

The equation proposed by Vanselow (5) differs from that of Kerr by the factor  $(\text{CaX}_2 + \text{NH}_4\text{X})$ :

$$\frac{(\text{NH}_4^+)^2 \text{CaX}_2 (\text{CaX}_2 + \text{NH}_4\text{X})}{(\text{Ca}^{++}) (\text{NH}_4\text{X})^2} = K \quad (B)$$

The values of  $K$  in table 4 are calculated by equation (B) from the data in table 2.

Vanselow used extracted soil colloids and concentrated salt solutions in his work, and consequently the suspensions were considerably different from the soils used in our work. Small differences in absorption would have comparatively much less effect on his results. On the one soil which he reports, the values of  $K$  were between 132 and 183. These values are much higher than those obtained in the present study, in which the concentrations were much

TABLE 4

Calculated values of  $K$  in the equation, 
$$\frac{(NH_4^+)^2(CaX_2)(CaX_2 + NH_4X)}{(Ca^{++})(NH_4)^2} = K$$

LABORATORY NUMBER	TOTAL EXCHANGE CAPACITY OF SOIL  <i>m.e.</i>	AMMONIUM SULFATE IN SOLUTION				POTASSIUM SULFATE IN SOLUTION		
		2.0 m.e.	4.0 m.e.	8.0 m.e.	16.0 m.e.	0.85 m.e.	4.0 m.e.	8 m.e.
12595	1.46	18,530.0	1,398.0	114.8	216.2			
12592	2.62	263.6	111.6	136.1	170.2			
20725	3.00	161.9	98.3	72.7	185.1	24.4	51.9	34.5
12597	3.08	460.5	185.2	169.1	642.1	46.1	150.7	148.0
18230	4.98	178.4	128.0	31.5	7.0			
12596	6.00	3,938.0	563.5	292.1	535.4	716.3	251.6	147.0
12647	6.44	60.8	34.3	53.8	76.1			
12652	11.30	100.0	62.7	51.9	69.1			
12518	13.71	1,819.0	375.8	137.1	120.5	234.3	120.2	69.7
12651	16.08	232.1	109.1	45.3	56.4			
9348	18.31	66.8	39.2	31.4	38.9	18.0	29.7	20.9
12519	18.49	242.5	114.5	75.9	105.7			
12642	18.70	1,592.0	100.4	84.6	103.3			
20721	21.28	28.0	44.5	57.4	42.8			
12659	23.43	318.9	87.2	65.6	69.5	167.5	64.3	61.8
12677	27.45	178.6	91.0	54.5	65.5	259.0	72.8	70.0
12581	27.60	39.9	49.2	38.8	32.3	65.5	29.1	13.2
12580	29.60	113.7	57.3	43.1	42.2	84.8	13.4	26.7
12533	37.24	805.4	67.6	32.4	30.0	153.9	18.7	19.6
18546	38.10	189.1	57.2	36.7	39.3			
7147	44.04	651.3	60.0	77.8	44.2	163.1	29.1	18.5
12571	44.13	418.6	76.9	97.2	98.8			
21067	45.81	104.0	35.3	32.0	31.8	68.9	33.2	17.4
18226	47.12	82.2	64.8	36.9	41.5			

lower. As with equation (A), the values of  $K$  vary with different soils, and with different concentrations of the absorbing material in the same soil.

In general, there is much less relative variation in the values of  $K$  by equation (B) than in those by equation (A). For many of the soils, the agreement between the values for a given soil for the 4, 8, and 16 m.e. solutions is fairly satisfactory; values for the 2.0 m.e. and 0.85 m.e. solutions are too high.

With soils of high exchange capacity in dilute salt solutions, the value of  $NH_4X$  is of very little importance, compared to the value of  $CaX_2$ . Under

these conditions, equation (B) of Vanselow amounts essentially to multiplying the value of  $K$  in equation (A) of Kerr by a constant  $\text{CaX}_2$ , the molecular concentration of the calcium exchange complex, which is equal to one-half the total exchange capacity. Equation (B) is then subject to the same objections as equation (A). On the whole, however, the introduction of the factor  $(\text{CaX}_2 + \text{NH}_4\text{X})$  tends to reduce materially the variations found in equation (A). Equation (B) is therefore considered by the writer to be better than equation (A). It is not good in the case of dilute salt solutions because the values of  $K$  are found to be too high.

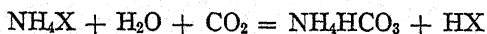
*Possible reasons for variations in values of K in Equations (A) and (B)*

The variations in the values of  $K$  presented in tables 3 and 4 may be due to a number of reasons. The simplest is perhaps of a mathematical nature, and holds where the quantity absorbed is less than 1. The square of this fraction is less than the original quantity. Since the square is used in the denominator of both equations (A) and (B), the resulting quotient will be larger than in cases where the original quantity is greater than 1. This increases the effect of small errors and might account for much of the apparently great variation of  $K$  with dilute solutions and soils of low exchange capacity.

A second reason may be found in differences in the nature of the exchange complexes of different soils. Such differences have already been suggested (table 2). Moreover, the exchange complex in a single soil may contain compounds which vary considerably in reactivity with bases in the solution. Consequently, at one level of reaction with a given base, a certain part of the exchange complex may be the principal absorbing compound, whereas at another level, a different compound may be the principal one, with a different state of equilibrium between soil and salt solution. It is also possible that we are dealing in this case with a complex saturated with various cations, including hydrogen ions.

The great effect of small variations in quantity of base absorbed upon the values of  $K$  has already been mentioned. Quantities of ammonium or potassium which are certainly within the range of experimental error are sufficient to cause considerable variation in the value of  $K$  when the total quantity absorbed is small, especially with dilute solutions and soils of low exchange capacity, where the principal variations of  $K$  occur. Experimental error may therefore be an important factor.

Another cause of variations in quantities of base absorbed is undoubtedly hydrolysis of the exchange complex. The total quantity of base absorbed is the result of an equilibrium between two reactions. The first is between the calcium complex and the base in the solution; the second is between the ammonium complex formed and the water as such or containing carbon dioxide:



A number of experiments were conducted in order to determine some of the factors involved in hydrolysis.

*Hydrolysis of the ammonium complex*

The relation between the total exchange capacity of various soils and the quantity of ammonium removed by hydrolysis was first determined.

Soils varying from 2.6 to 39 m.e. in exchange capacity were selected and were completely saturated with ammonium. Ten grams were leached with 250 cc. of neutral normal ammonium acetate. The excess ammonium acetate was then washed out of the soil with ethyl alcohol. It was very difficult to be certain that all of the excess ammonium had been removed, since the presence of alcohol greatly reduced the sensitivity of the Nessler test. Although a slight excess of ammonium might not be significant in the estimation of total exchange capacity, it was of great importance in this experiment where very

TABLE 5

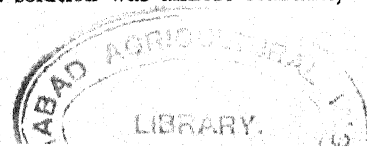
*Ammonium hydrolyzed from soils previously treated with ammonium salt solutions in ways indicated*

LABORATORY NUMBER	TOTAL EXCHANGE CAPACITY OF SOIL	AMMONIUM HYDROLYZED FROM COMPLEX SATURATED WITH AMMONIUM		AMMONIUM ABSORBED AND HYDROLYZED FROM SOILS TREATED WITH 2 M.E. $(\text{NH}_4)_2\text{SO}_4$ SOLUTION		
				Absorbed	Hydrolyzed	
	m.e.	m.e.	per cent	m.e.	m.e.	per cent*
12592	2.62	0.59	22.4	0.33	0.40	121
20724	4.13	0.50	12.1	0.35	0.26	80
18230	4.98	0.76	15.2			
12596	6.00	0.90	15.0	0.24	0.24	100
18539	12.69	0.82	6.5			
9347	18.13	1.38	7.6	1.00	0.37	37
12519	18.49	1.46	7.9	0.93	0.54	58
12642	18.70	0.66	3.5	0.60	0.46	77
20721	21.28	0.96	4.5	1.41	0.51	36
21071	26.38	1.00	3.8	1.25	0.40	32
12677	27.35	1.02	3.7	1.15	0.53	46
21072	38.80	1.00	2.6			

\* Per cent of that absorbed.

small quantities of ammonium were involved. On the other hand, excessive washing might cause some hydrolysis with removal of some of the ammonium combined with the exchange complex. No satisfactory test for the determination of the end point of the washing was developed. The soil was washed with alcohol three or four times after a negative Nessler test, transferred to bottles, and 40 cc. of ammonia-free water added. The bottles were shaken for 1 hour on an end-over-end shaking machine. The soil was then filtered off, and ammonium was estimated in an aliquot of the filtrate by the Nessler method.

The results are given in the third column of table 5. The quantity of ammonium in solution varied with different soils but the increase was not in direct proportion to the exchange capacity of the soil. After the total exchange capacity exceeded 6 m.e., the ammonium in solution was almost constant,



being about 1 m.e. The percentage of ammonium hydrolyzed decreased from 22.4 to 2.6 as the exchange capacity increased. These results strongly indicate that the quantity of ammonium brought into solution by hydrolysis of the base exchange complex may be related more closely to the volume of the water present than to the base exchange capacity.

Another test was made to ascertain the amount of hydrolysis when only part of the bases of the exchange complex were replaced by ammonium.

Two 10-gm. samples of nine soils were shaken for 1 hour with 40 cc. of solution containing ammonium sulfate equivalent to 2 m.e. per 100 gm. of soil. The solution was then filtered off and the soil washed free of excess ammonium sulfate with ethyl alcohol. The samples were then suspended in 40 cc. of ammonia-free water, shaken for 1 hour, filtered, and the ammonium in solution determined by the Nessler method. The results are presented in the last columns of table 5. The quantities of ammonium absorbed are to some extent related to the exchange capacity of the soils. The quantity of ammonium removed from the soil by hydrolysis was nearly constant, especially with the last six soils in the table, although the total exchange capacity and the quantity of ammonium absorbed varied considerably. Perhaps the most interesting soil in this connection is No. 12642. Although it absorbed considerably less ammonium than could have been expected from the total exchange capacity, the quantity of ammonium from this soil by hydrolysis is practically the same as for the other soils.

A third experiment was conducted in which a constant amount of 1.0 m.e. of exchange complex was used from different soils. The same soils were used as those listed in table 2, but only 10 per cent as much. In all but two of the soils, the quantity of ammonium hydrolyzed was practically identical, varying from 1.13 to 1.35, and averaging 1.23 m.e., or 12.3 per cent of the total present. Soils 12642 and 20721 gave low results, 0.96 m.e. and 0.93 m.e. respectively.

The effect of the volume of water upon the hydrolysis of the base exchange complex was tested because the volume of water was apparently of importance. The base exchange complexes of 10-gm. lots of soils Nos. 12596, 18539, 12642, and 20721 were saturated with ammonium from ammonium acetate as has been described, washed, and shaken with 20, 40, 80, and 160 cc. portions of water. The m.e. of ammonium in solution were as follows: for 20 cc. of water, 0.82, 0.71, 0.78, and 0.80; for 40 cc. of water, 0.90, 0.82, 0.66, and 0.98; for 80 cc. of water, 1.30, 1.24, 1.40, and 1.35; for 160 cc. of water, 1.38, 1.20, 2.81, and 2.59. For the first two volumes, the amount of ammonium hydrolyzed was practically identical for all the soils. With the 80 cc. of water, the ammonium hydrolyzed was appreciably higher than with the 20 cc. or 40 cc. With the 160 cc., or a ratio of 1:16, solutions from soils Nos. 12642 and 20721 contained twice as much ammonium as those from Nos. 12596 and 18539.

The results presented show that hydrolysis occurs and that it plays a relatively more important rôle with soils of low exchange capacity than with those of high exchange capacity. When the quantity of base in the salt solution is



low, the quantity hydrolyzed may be relatively large when compared with the total quantity absorbed by the soil. A part of the variations in the values of the constant  $K$  in equations (A) and (B) is undoubtedly due to hydrolysis.

#### *Adsorption equation of Csiky*

The three equations now to be considered are based upon adsorption, instead of equilibrium in accordance with the mass law upon which equations (A) and (B) are based. The first of these is that proposed by Vageler and Woltersdorf (4) and Csiky (1):

$$y = \frac{x \cdot S}{x + C} \quad (C)$$

where  $x$  = the quantity of reagent used for ion exchange,  $y$  = the exchanged ions found,  $S$  = the limiting value of the absorption capacity. If reciprocal values are used, the graph becomes a straight line, of the formula

$$\frac{1000}{y} = \frac{1000}{S} + q \frac{1000}{x}$$

where  $q$  is the slope of the curve, determined by the data of two determinations with solutions of different concentrations, which give two points on the curve. The values for  $q$  and  $S$  were calculated from data presented in table 1, and are given in table 6. The values for  $q$  are fairly constant in practically all of the soils. The agreement between the several values is much better than that for  $K$  in either equation (A) or (B). However, the value of  $q$  is somewhat variable for soils of low exchange capacity and dilute solutions. The quantities absorbed are still too small to fulfill the requirements of equation (C).

The values of  $S$  were calculated for the value of  $q$  between 8 and 16 m.e. of ammonium sulfate, and the values of  $x$  and  $y$  for 16 m.e. The values of  $S$  represent the limiting values of the absorption capacity. They are presented in the fifth column of table 6 with the total exchange capacities for comparison in the sixth column. The agreement between the value of  $S$  and the total exchange capacity is fairly good for 18 of the 24 soils, but not so good with the other 6. In many cases, the agreement between the calculated value and the laboratory determination is within the range of experimental error.

In order to estimate the magnitude of the variation of values of  $q$  and  $S$  with dilute solutions, the values of  $y$  when  $x = 2$  were calculated from the data for  $x = 16$ ; the determined values of  $y$  were subtracted from the calculated values of  $y$ . The differences are given in the last column of table 6. In most cases, the differences are small and within the experimental error.

Values of  $q$  and  $S$  for the potassium data are also given in table 6. The values of  $q$  vary from 1.20 to 3.54 but are somewhat more constant than those for ammonium. Values of  $S$  for most of the soils agree closely with the values for total exchange capacity, but in soils Nos. 12533 and 7147, they are much too large.

Values of  $q$  for the data presented in table 2 (absorption of ammonium by a constant quantity of exchange complex) varied from 2.06 to 2.88, with an average of 2.36. Values of  $S$  varied from 7.15 (No. 12642 with very low absorption of ammonium) to 10.84, the average being 9.08, instead of the 10.0 used.

TABLE 6

Values of  $q$ ,  $S$ , and  $y$  in the equation  $\frac{1000}{y} = \frac{1000}{S} + q \frac{1000}{x}$

LABORATORY NUMBER	<i>q</i>			<i>q</i>	<i>S</i> FOR AMMO- NIUM	TOTAL EXCHANGE CAPACITY	<i>S</i> FOR POTAS- SIUM	DIFFERENCE BETWEEN CALCULATED AND DETERMINED VALUE OF <i>y</i>
	Ammonium			Potassium				
	2-4 m.e.	4-8 m.e.	8-16 m.e.	0.85-8.0 m.e.				
						<i>m.e.</i>		
12595	48.48	25.25	3.65		1.07	1.48		0.30
12592	6.24	4.00	4.04		2.26	2.62		0.08
20725	4.56	4.26	1.89	2.06	5.01	3.00	2.91	0.08
12597	6.75	4.76	1.76	2.20	1.40	3.08	1.54	0.31
18230	4.00	3.44	3.45		4.25	4.98		0.02
12596	10.96	5.34	2.93	3.54	2.76	6.00	5.81	0.30
12647	2.43	1.69	2.17		5.71	6.44		0.00
12652	2.08	1.99	1.82		9.87	11.30		0.09
12518	5.01	3.34	2.31	1.96	11.48	13.71	13.25	0.32
12651	2.25	2.33	1.62		14.56	16.08		0.25
9348	1.65	1.57	1.47	1.21	18.12	18.31	14.10	0.08
12519	2.17	1.98	1.62		12.27	18.49		0.19
12642	4.60	2.01	1.34		10.34	18.70		0.71
20721	1.52	1.51	1.49		22.03	21.28		0.00
12659	2.25	1.69	1.57	1.53	19.19	23.43	17.85	0.22
12677	1.74	1.67	1.45	1.57	22.08	27.35	24.40	0.15
12581	1.21	1.45	1.43	1.32	29.67	27.60	30.30	0.12
12580	1.57	1.47	1.45	1.32	34.48	29.60	32.25	0.06
12533	2.61	1.52	1.29	1.37	37.74	37.24	250.00	0.52
18546	1.68	1.48	1.31		38.17	38.10		0.20
7147	2.29	1.36	1.28	1.33	42.55	44.04	143.0	0.43
12571	1.95	1.24	1.47		36.50	44.13		0.14
21067	1.44	1.23	1.26	1.20	51.30	45.81	66.6	0.09
18226	1.25	1.40	1.26		44.20	47.12		0.03

Equation (C) gives fairly constant values of  $q$  for all soils; the values of  $S$  agree fairly well in nearly all soils with the total exchange capacity and with the quantities of ammonium and potassium absorbed. It appears to be a fairly satisfactory equation.

#### *Absorption equation of Patten and Waggaman*

On the basis of early work, conducted before the development of modern concepts concerning exchange capacity, Patten and Waggaman (3) suggested

that the absorption of a base by a soil followed a curve which may be expressed by the differential equation:

$$\frac{dy}{dv} = K(A - y) \quad (D)$$

Upon integration and changing to Briggsian logarithms, equation (D) becomes

$$\text{Log } (A - y) - \text{log } A = -Kv.$$

TABLE 7

Values of 1000 K in the equation  $\frac{dy}{dx} = K(A - y)$

LABORATORY NUMBER	AMMONIUM SULFATE IN ORIGINAL SOLUTION				POTASSIUM SULFATE IN ORIGINAL SOLUTION		
	2 m.e.	4 m.e.	8 m.e.	16 m.e.	0.85 m.e.	4 m.e.	8 m.e.
12595	9.2	17.8	36.9	24.1			
12592	29.3	32.6	27.1	21.7			
20725	31.4	32.2	31.1	19.7	49.7	39.3	32.2
12597	23.1	25.7	22.9	13.4	54.2	27.6	24.0
18230	24.4	27.9	31.7	49.6			
12596	8.9	13.5	14.1	9.8	20.0	17.2	17.3
12647	28.1	29.2	23.2	18.8			
12652	18.3	18.1	17.0	15.7			
12518	7.9	10.5	11.7	10.3	15.6	11.2	14.0
12651	12.4	12.8	14.2	12.6			
9348	14.3	14.6	14.1	12.6	19.0	15.7	15.4
12519	11.0	11.7	11.5	9.5			
12642	7.1	11.9	12.3	9.5			
20721	15.0	12.9	11.2	11.2			
12659	9.2	10.6	10.3	9.1	12.0	11.8	10.3
12677	9.3	9.5	9.5	8.5	10.0	9.5	9.1
12581	11.7	10.5	10.1	9.5	12.1	11.4	2.1
12580	9.5	9.7	9.5	9.0	10.9	11.8	10.3
12533	5.8	8.0	8.4	7.8	8.6	11.9	9.1
18546	7.3	8.1	8.1	7.6			
7147	5.4	7.2	7.1	6.7	7.5	7.8	7.7
12571	5.8	6.9	6.2	5.7			
21067	7.0	7.9	7.2	6.9	7.9	7.5	7.7
18226	7.0	7.9	7.5	6.7			

If the volume be kept constant, the term  $v$  may be replaced by the concentration,  $x$ , of the solution used. The equation states that the rate of change in quantity absorbed with the change in quantity of salt used is proportional to that part of the exchange complex not already combined with the base concerned. Values of  $K$  calculated for the data given in table 2 are given in table 7.

The values of  $K$  for soils of low exchange capacity are relatively high. For the same soil, there is very good agreement in the values of  $K$  for solutions of

different concentrations. The values for potassium are very similar to those for ammonia, indicating that minor differences in absorption are not greatly magnified in this equation. The values of  $K$  vary with different soils, tending to decrease as their exchange capacity increases.

*Adsorption equation of Wiegner*

The relationship between the concentration of an ion in the solid phase—the soil—and the concentration in solution at equilibrium has been held by G. Wiegner (6) to be identical with the Freundlich adsorption equation:

$$y = KC^{1/p} \quad (E)$$

where  $y$  is the amount in unit weight of soil, including that originally present,  $C$  the concentration of the ion in solution, and  $K$  and  $p$  are constants. By changing equation (E) from the exponential to the logarithmic form, the following equation is obtained:

$$\text{Log } y = \text{Log } K + 1/p \log C.$$

This is a straight line equation in which  $\log y$  is plotted against  $\log C$ ,  $K$  is the quantity of ammonia adsorbed when  $C = 1$ , and  $1/p$  is the slope of the curve so constructed. Curves were constructed on this basis. In practically all soils, the values as plotted fell on a smooth curve, so that it was possible to interpolate accurately for the values of  $K$  and calculate those of  $p$ . Values of  $K$  and  $p$  are given in table 8.

In equation (E), no account is taken of the total exchange capacity, since the only variables are the quantities of the ion absorbed and that in solution. If the value of  $K$ , that is, the total quantity in the soil at unit concentration in solution, be divided by the number of units of total exchange capacity,  $T$ , the result will be the quantity of ion taken by a unit of exchange capacity when a unit of ion is in solution. This is perhaps one of the best possible ways of obtaining comparative data for the absorption reactivity of the complexes of different soils. This quantity was calculated and is given in the fourth and ninth columns of table 8. The values of  $K/T$  differ considerably in the various soils and also for ammonium and potassium. An average of the same 12 soils gave  $K/T$  a value of 0.0620 with ammonium and 0.0851 with potassium. The value of  $p$  was practically constant with all of the soils; there was no difference between ammonium and potassium in this respect. By using the average values, equation 4 can be changed to read

$$y = .0648 T C^{.77} \text{ (ammonium)}$$

$$y = .0851 T C^{.77} \text{ (potassium)}$$

In cases where the final concentration is low, the exponent is so nearly 1 that it is of comparatively little importance. If it be disregarded, equation (E) may be used to calculate the quantity of ammonium which would be absorbed when a given amount,  $B$ , is applied to the soil. Under conditions similar to

those in the experimental work reported in this paper, equation (E) may be rearranged to give:

$$y = \frac{.0648 T B}{1 + .0648 T}$$

With this equation,  $y$  was calculated for ammonium when  $B = 2$  and (by the use of  $.0851T$  instead of  $.0648T$ ) for potassium when  $B = 0.85$ . The calculated

TABLE 8  
Calculated values of constants in equation  $y = KC^{1/p}$

LABORATORY NUMBER	TOTAL EXCHANGE CAPACITY (T)	AMMONIUM			AMMONIUM ABSORBED FROM 2 M.E. SOLUTION		POTASSIUM			POTASSIUM ABSORBED FROM 0.85 M.E. SOLUTION	
		K	K/T × 100	P	Calcu- lated	Found	K	K/T × 100	P	Calcu- lated	Found
					m.e.	m.e.				m.e.	m.e.
12595	1.46	0.025	1.73	1.20	0.17	0.06					
12592	2.62	0.25	9.54	1.45	0.29	0.33					
20725	3.00	0.30	9.99	1.60	0.33	0.41	0.54	18.00	1.75	0.18	0.36
12597	3.08	0.29	8.97	1.45	0.33	0.31	0.41	13.30	2.15	0.18	0.31
18230	4.98	0.36	7.24	1.05	0.49	0.53					
12596	6.00	0.23	3.93	1.10	0.55	0.24	0.34	5.66	1.20	0.30	0.23
12647	6.44	0.49	7.62	1.10	0.59	0.79					
12652	11.30	0.91	8.00	1.25	0.85	0.91					
12518	13.71	0.39	2.85	1.20	0.94	0.49	0.86	6.25	1.15	0.47	0.42
12651	16.08	0.91	5.64	1.25	1.02	0.89					
9348	18.31	1.38	7.56	1.30	1.04	1.18	2.00	10.91	1.55	0.53	0.67
12519	18.49	0.98	5.30	1.25	1.09	0.93					
12642	18.70	1.36	7.30	1.55	1.09	0.60					
20721	21.28	1.91	9.01	1.65	1.16	1.41					
12659	23.43	1.32	5.68	1.25	1.21	0.97	1.35	5.75	1.30	0.58	0.54
12677	27.45	1.41	5.09	1.10	1.27	1.15	1.39	5.05	1.20	0.61	0.53
12581	27.60	2.08	7.58	1.40	1.28	1.44	2.46	8.93	1.15	0.61	0.64
12580	29.60	2.09	7.12	1.50	1.31	1.27	2.14	7.23	1.05	0.62	0.63
12533	37.24	2.08	5.61	1.05	1.42	0.97	2.53	6.78	1.05	0.65	0.62
18546	38.10	2.24	5.82	1.35	1.44	1.27					
7147	44.04	2.38	5.41	1.15	1.45	1.08	2.88	6.55	1.05	0.68	0.64
12571	44.13	2.32	5.40	1.60	1.48	1.17					
21067	45.81	3.01	6.57	1.40	1.51	1.45	3.62	7.67	1.15	0.69	0.70
18226	47.12	2.64	5.60	1.40	1.51	1.50					
Average (24 soils).....		1.31	6.48	1.32	0.99	0.89					
Average (12 soils).....			6.20	1.30	1.05	0.91		8.51	1.31	0.51	0.53

quantities, compared with those found by experiment, are given in four columns of table 8 under the respective headings of ammonium and potassium. In most cases, the differences between "calculated" and "found" are within the experimental error. The average quantity of ammonium calculated was 11 per cent greater and the average potassium 4 per cent smaller than that found.

Equation (E) gives values which agree excellently with the experimental data. It is a good method for comparing quantitatively the absorption capacity of the exchange complexes of different soils. For practical use and without regard to the theories involved, equation (E) is probably the best of all of the equations studied.

#### SUMMARY

Five mathematical equations expressing the relations between total exchange capacity and the absorption by soils of ammonium and potassium from solutions of ammonium sulfate and potassium sulfate were studied in order to determine which equation gave values in best accordance with experimental results. The results of the study may be summarized as follows:

Quantities of base absorbed varied approximately with the total exchange capacity. However, marked differences were evident in the quantity of base absorbed by soils of similar exchange capacity from identical solutions. These were probably due to the relative importance of capillary absorption and to differences in the compounds making up the exchange complex.

The simple mass law equilibrium equation,  $(\text{NH}_4^+)^2 (\text{CaX}_2) / (\text{Ca}^{++}) (\text{NH}_4\text{X})^2 = K$ , gave values for the proportionality constant,  $K$ , which were too high with soils of low exchange capacity and solutions of low concentration.

The mass law equilibrium equation in which the theory of mixed crystals is introduced,  $(\text{NH}_4^+)^2 (\text{CaX}_2) (\text{CaX}_2 + \text{NH}_4\text{X}) / (\text{Ca}^{++}) (\text{NH}_4\text{X})^2 = K$  gave somewhat better agreement between the values of  $K$  than the preceding equation, but was not good with some of the conditions under which the simple mass law equation held.

Values calculated for the adsorption equation  $y = xS/(x + C)$  were comparatively uniform. Values of  $y$  as calculated agreed fairly closely with the quantity of ammonium absorbed. Values of  $S$ , the adsorptive limiting value of the equation, agreed fairly well with the total exchange capacity. The equation is fairly satisfactory.

Values of  $K$  calculated according to the differential equation  $dy/dx = K(A - y)$  were fairly uniform for a given soil and solutions of different concentrations. The values were somewhat higher with soils of low exchange capacity.

The equation  $y = KC^{1/p}$  gave values which are in best accord with the values determined experimentally. The value of  $K$ , when divided by the total exchange capacity,  $T$ , gave a quotient which was fairly similar for all soils. It indicated, however, significant differences in the absorptive capacity of some soils per unit of exchange complex. The values of  $p$  were practically constant for all soils. The equations best fitting the general data were  $y = .0648 TC^{.77}$  for ammonium and  $y = .0851 TC^{.77}$  for potassium.

#### REFERENCES

- (1) CSIKY, J. S. 1932 On the determination of the ion exchange capacity of soils. *Soil Sci.* 34: 269-279.
- (2) KERR, H. W. 1928 The identification and composition of the soil alumino-silicate active in base exchange and soil acidity. *Soil Sci.* 26: 385-398.
- (3) PATTEN, H. E., AND WAGGAMAN, WM. H. 1908 Absorption by soils. U. S. Dept. Agr. Bur. Soils Bul. 52.
- (4) VAGELER, P., AND WOLTERS DORF, J. 1930 Beiträge zur Fragen des Basenaustausches und der Aziditäten. *Ztschr. Pflanzenernähr. u. Düngung (A)* 15: 329.
- (5) VANSELOW, ALBERT P. 1932 Equilibria of the base-exchange reactions of bentonite, permutites, soil colloids, and zeolites. *Soil Sci.* 33: 95-113.
- (6) WIEGNER, G. 1912 Zum Basen austausch in der Ackererde. *Jour. Landw.* 60: 110-157.

# SOIL TEMPERATURE APPARATUS FOR FIELD WORK

G. ALLEN MAIL

Montana Agricultural Experiment Station

Received for publication November 30, 1934

In connection with some work on the development of grasshopper eggs in nature, during the unseasonably warm spring of 1934, the writer had occasion to collect many soil temperature data. It was, of course, necessary to leave the ground undisturbed in order to obtain accurate temperature readings. Some of the readings made on shaded slopes involved the penetration of frozen surface soil in which the usual types of soil thermometer could only be employed with difficulty. Furthermore these soil thermometers could not be readily used for temperatures at depths below six inches. For these reasons a thermocouple constructed as described was found to be most satisfactory.

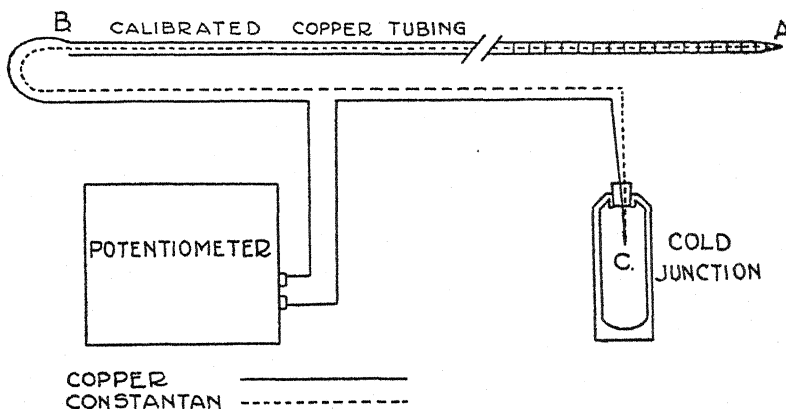


FIG. 1. SOIL TEMPERATURE APPARATUS

A piece of thick-walled copper tubing having an outside diameter of  $\frac{3}{16}$  inch and 15 inches in length was hammered out to a taper point. A well-insulated 28-gauge constantan wire was drawn through the tube, and its end was welded to the tapered point (A) as illustrated (fig. 1). The tube was then filled with insulating compound. To the other end of the tube was soldered an insulated 28-gauge copper wire (B). The copper and constantan wires were encased in rubber tubing for a foot or two beyond the copper tubing as a measure of protection. Beyond the rubber tubing a second thermocouple (cold junction) was made (C), and the set-up was ready for use with a potentiometer. By filing half or quarter inch divisions on the tube, it could be readily forced

into the ground to any desired depth within its range and the temperature at its tip be quickly recorded.

The thermocouple potentiometer used in the field was a General Electric type PJ-1B. As this particular instrument has a built-in galvanometer and a temperature compensator it is unnecessary to carry an outside galvanometer or a thermos flask of cracked ice for the cold junction, but these might be needed with some makes of galvanometers such as the Leeds and Northrup Pyrovolter.

With this apparatus it is possible to measure a temperature gradient in most situations involving soil temperature much more speedily than is possible by the use of the standard soil thermometer in general use.



# CORROSIVENESS OF CERTAIN OHIO SOILS<sup>1</sup>

I. A. DENISON AND S. P. EWING

*Bureau of Standards, U. S. Department of Commerce*

Received for publication December 15, 1934

Recognition of the fact that pipe lines laid in certain areas are seriously corroded by contact with the soil, while in other areas they are relatively unaffected, has resulted in the development of a variety of methods for predicting the corrosive action of soils. The procedure usually followed in these methods consists in testing the soil in place at more or less arbitrary intervals along a right-of-way, and in indicating from the results those sections where corrosion will be severe and hence where protection of the pipe line will be required. Instead of testing the soil in place, samples of soil may be taken at definite points and examined in the laboratory. In either procedure, no effort is made to classify and to fix the boundaries of the types of soil which occur along the prospective pipe line.

For a corrosion survey to have wide application and to be made economically, the determination of the corrosiveness of each soil type is essential. Once the corrosiveness of each soil type has been definitely established, the extent of corrosion that will probably be encountered along a pipe line passing through these soils can be estimated by identifying the soils and fixing their boundaries. The purpose of this study was to determine whether the corrosiveness of certain soil types is sufficiently well defined to be of practical use in corrosion surveys. If so, it should be possible to estimate the corrosiveness of other soils by correlating certain properties of the soil types with their corrosiveness.

## SOURCE OF CORROSION DATA

The field work of this investigation was conducted along the right-of-way of a group of parallel pipe lines in northern Ohio. A correlation between the repairs which have been made on a 32-mile section of these lines and the eight types of soil occurring along the lines has been previously shown by one of the authors (1). In the present study the scope of this preliminary work was extended to approximately 200 miles, and the number of soil types identified was increased to 35.

<sup>1</sup> The investigation of pipe line corrosion, of which the work described in this paper is a part, is a project of the American Gas Association. The staff of the National Bureau of Standards cooperated in certain phases of the work.

Publication approved by the Director of the National Bureau of Standards, U. S. Department of Commerce.

Data on the corrosiveness of the soils were obtained from the record of repairs made on the pipe lines from the time of their installation to the present, a period of approximately 45 years. This record is based upon the actual leaks which have occurred in operating the lines. When a leak occurs it is repaired temporarily and the exact location and date of repair is recorded. Experience has shown that when several leaks have occurred on a short section of the line more leaks can be expected and that they will occur with increasing frequency. Finally, when the accumulation of leaks indicates the necessity of reconditioning, the pipe is uncovered and repaired by spot welding the pits and patching the larger corroded areas. The repair crew then works along the line in both directions until in the judgment of the foreman further uncovering and repair work are unnecessary. The fact that most of the reconditioning was done on short sections, *e.g.*, a few hundred feet, indicates that the work was done only when necessary. Although the repair record can not be considered a precise measure of the corrosion that has occurred, it has the advantage of a long time experiment, in which the effects of seasonal variation and accidental causes of failure, such as defective pipe, are minimized.

#### DESCRIPTION OF SOILS

In the extreme western part of Ohio the pipe lines are in the region of glacial limestone soils, the Clyde, Brookston, Crosby, and Miami soils being the most widely distributed along the lines. Proceeding eastward, the lines enter the glacial lake region of northwestern Ohio, in which the soils are derived from both glacial and lacustrine material. In this region the soils could be readily classified in well-recognized series with the exception of certain soils which, although similar to the Wauseon soils, differed from the latter in having a yellowish brown heavy subsoil instead of the darker sandy subsoil typical of the true Wauseon. Because of this difference and also the fact that glacial till occurred at a relatively shallow depth (24 inches) the soils were tentatively classified as "Wauseon-like" soils.

The pipe lines in the eastern part of Ohio lay wholly in the region of glacial soils derived from sandstone and shale. The predominant glacial soils in this region belong to the following series: Wooster, Canfield, Ellsworth, Mahoning, and Trumbull. The terrace and flood plain soils occurring most extensively are those of the Chenango, Braceville, Chagrin, and Holly series.

#### METHODS

##### *Field work*

The field work consisted in identifying and mapping the soil types along the pipe lines. Borings were made where there was any question as to the soil type, and samples were taken when necessary, depending largely upon the variations that were found in the soils. At many locations a sample was taken of the soil in each horizon of the profile to a depth of 30-36 inches. Usually, however, a single sample was taken from the middle or B-horizon in which the pipe lines were usually found. The soil types were indicated on the topo-

graphic map with appropriate symbols, and features which appeared to be significant were recorded in the notes. Distances from known stations were measured by pacing. About 8 miles of line per day could be surveyed in this manner. In order to avoid the possibility of bias in mapping the soils the record of repairs was not examined until after the completion of the survey.<sup>2</sup>

#### *Estimation of total acidity of soils*

The laboratory work was limited to measurements of the total acidity and resistivity, since these properties appear to be most closely related to the corrosiveness of soils (3, 4). The acidity was measured by a modification of the titration method described by Denison (2). A 5-gm. portion of the air-dry soil, which had been passed through a 20-mesh sieve, was placed in each of two test tubes (25 × 200 mm.) and 25 ml. of *N* NaCl solution was added to each tube. One milliliter of 0.2 *N* Na<sub>2</sub>CO<sub>3</sub> was pipetted into one tube and 2 ml. into the other. The pH of the solution in the more alkaline tube was then determined colorimetrically, cresol red being used as the indicator. If the pH was below 7.2, the lower limit of the indicator, 2 ml. more of the carbonate solution was added to each tube and the process was repeated until the pH of the more alkaline solution was above 8. The tubes were allowed to stand with occasional shaking until the solutions were in equilibrium with the soil and showed no further change of pH with time. The amount of alkali required to bring the soil to pH 8 was then determined by interpolation or extrapolation, the titration curve being assumed to be a straight line for the short distance between the two pH values. For a 5-gm. sample, 1 ml. of 0.2 *N* Na<sub>2</sub>CO<sub>3</sub> solution is equivalent to 4 m.e. of hydrogen ion per 100 gm. of soil. The titration was made to pH 8 because the points of inflection in the titration curves for a large number of soils were found to be near this value (2). Although the results by this method are not accurate to better than 1 m.e. of acid per 100 gm. of soil, they are sufficiently close for the purpose, because acidity measurements of samples taken adjacent to each other in the field frequently vary by more than this amount.

From the values for acidity and resistivity of the individual samples the average acidity and resistivity of each soil type was calculated. In the case of those locations in which samples were taken from the different horizons, the average acidity and resistivity of the horizons, weighted according to their thickness, were used in computing the average values for the soil types.

#### PROPERTIES AND CORROSIVENESS OF SOIL TYPES

The total acidity and resistivity of each soil type together with the approximate standard deviations of the means<sup>3</sup> are shown in table 1.

<sup>2</sup> The authors are indebted to Dr. G. W. Conrey of the Ohio Agricultural Experiment Station and to Mr. A. E. Taylor of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, for suggestions concerning the identification of the soils.

<sup>3</sup> Standard deviation of the mean =  $\sigma M = \frac{\sigma X}{\sqrt{n-1}}$  (approximately) where  $\sigma X$  = standard deviation of individual results,  $\sigma M$  = standard deviation of mean = standard error,  $n$  = number of observations.

It is apparent from the magnitude of the standard deviations of the mean and from the numbers of samples that the average values given for the different

TABLE 1  
*Summary of soil acidity and resistivity measurements*

SYMBOL AND SOIL TYPE	NUM- BER OF SAM- PLES	ACIDITY (M.E. PER 100 GM.)		RESISTIVITY (OHM-CM. AT 60°F.)	
		Mean	Stand- ard devia- tion of mean	Mean	Stand- ard devia- tion of mean
A <sub>1</sub> Clyde clay loam 1st section.....	13	14.6	1.5	2,758	224
A <sub>2</sub> Clyde clay loam 2nd section.....	3	14.0	1.9	2,983	112
B Braceville loam.....	2	15.0	...	9,410	...
Bc <sub>1</sub> Brookston clay loam 1st section.....	25	14.2	0.9	3,051	215
Bc <sub>2</sub> Brookston clay loam 2nd section.....	7	14.0	2.7	2,965	600
C Caneadea silt loam and fine sandy loam.....	8	12.7	2.1	4,329	837
Ca Canfield silt loam.....	7	18.7	1.6	9,773	1,037
Ch Chagrin Silt loam and fine sandy loam.....	15	12.6	1.0	6,184	675
Ci Cinders.....	6	14.6	4.0	2,081	160
Cs <sub>1</sub> Crosby silt loam 1st section.....	19	22.0	1.2	4,337	260
Cs <sub>2</sub> Crosby silt loam 2nd section.....	2	19.0	...	5,660	.....
D Chenango silt loam.....	2	9.5	...	8,320	.....
E Ellsworth silt loam.....	5	20.4	2.5	7,134	1,880
G Genesee silt loam.....	7	7.3	1.0	2,661	512
H Holly clay loam.....	10	26.7	2.4	3,100	763
K Lorain fine sandy loam.....	1	7.0	...	4,400	.....
Kc Lorain clay loam.....	5	14.0	3.2	3,489	321
L Lordstown fine sandy loam.....	2	16.5	...	11,450	.....
Ll Millsdale and other shallow limestone soils.....	..	....	....	....	....
Lf Lucas fine and very fine sandy loams.....	2	6.7	...	7,210	.....
M Mahoning silt loam.....	37	18.1	0.7	4,903	475
Ms Miami clay loam, silt loam, and fine sandy loam..	17	16.8	2.8	3,982	452
Mu Muck.....	1	36+	...	2,070	.....
N Nappanee clay loam.....	3	17.5	3.6	1,009	350
Nf Newton fine sandy loam.....	1	8.0	...	2,820	.....
P Plainfield fine sand includes gravelly phase.....	2	6.7	...	6,720	.....
S Undifferentiated sands and sandy loams.....	1	8.0	...	2,990	.....
T Trumbull clay loam and silt loam.....	8	21.1	2.3	4,455	720
Ti Till (some Allis and Chenango).....	6	9.3	5.6	2,525	920
V Volusia silt loam.....	30	17.2	1.0	5,473	383
VI Volusia loam.....	5	10.4	1.3	6,023	603
Wf Wooster fine sandy loam.....	2	14.7	...	6,442	2,718
Wl Wooster loam.....	13	15.5	1.6	8,002	1,010
W Wauseon fine sandy loam.....	2	7.5	...	4,248	.....
Wa "Wauseon-like" soils.....	1	8.0	...	694	.....

soils are not equally reliable. Thus the average acidity and resistivity of an extensive soil type, such as the Mahoning silt loam, is known with a high degree of precision because a large number of samples of such soils were taken. On

the other hand, little reliance can be placed upon the values for soils present to a limited extent along the pipe line, since they are represented by so few samples.

It will be noted that the data for three soils; namely, the Clyde clay loam, the Brookston clay loam, and the Crosby silt loam, have been separated into two groups for which, however, the respective acidities and resistivities are practically the same. This separation was suggested by the fact that the extent of repairs differs greatly in areas of each of these soil types depending upon their position with respect to a certain division point on the pipe line. West of this division point, where the soils are more corrosive, the pipe lines parallel a railroad for many miles. It is possible that the accumulation of cinders on the surface of the soils might account for their greater corrosiveness in this region.

The essential data on the corrosion of the pipe lines are given in table 2. The repairs which have been made in the different soils are expressed both as percentage per area and percentage of the total length of line in each soil type. According to the first method of expressing the data the repairs in the various bodies are simply averaged without regard to the size of the area. The standard deviation of the percentage of pipe repaired in each type (column 4) was obtained by weighting the percentages for each separate area according to the length of line in that area. The standard deviation of the mean (column 8) was also calculated for the separate areas. Since this value varies inversely with the square root of the number of observations it does not give a true idea of the accuracy of the mean in the case of those soils which occurred in a few large bodies.

The data of table 2 show that although there is considerable spread in the amount of pipe replaced in various areas of the same soil type, there are consistent differences in the corrosiveness of the various types. Thus among the most corrosive soils must be listed the Clyde clay loam 1st section ( $A_1$ ), soil overlaid by cinders (Ci), the Nappanee clay loam (N), and the "Wauseon-like" soils (Wa). On the other hand, the Canfield (Ca), Lordstown (L), and Wooster (Wl) silt loams and the large group of undifferentiated sands and sandy loams (S) must certainly be considered non-corrosive. The certainty with which the corrosiveness of the different soils is known depends upon the extent to which the soils occur along the pipe lines. For instance, relatively little weight can be given to the value for the Lorain fine sandy loam (L) since only one-half mile of this soil was mapped.

Further examination of table 2 shows that the repairs in small bodies of a given soil type are more likely to differ from the average of that type than are the repairs in larger bodies. It will be observed that in general the standard deviations of the percentage repaired per body of soil (column 7) are greater than the deviations calculated from the total length of line repaired in that soil (column 4). Errors in mapping the type boundaries and in locating the places where repairs were made in small bodies of soil introduce larger errors than in a single body of equal area.

The wide spread in the data summarized in table 2 may be illustrated by the repairs in a single soil type. In table 3 are shown the repairs in five bodies of the Lordstown sandy loam.

TABLE 2  
*Summary of data on pipe line repairs*

SOIL TYPE	LENGTH OF LINE IN HUNDREDS OF FEET	PERCENTAGE OF PIPE REPAIRED	STANDARD DEVIATION OF PERCENTAGE REPAIRED $\sigma_X$	NUMBER OF BODIES	AVERAGE PERCENTAGE REPAIRED PER BODY	STANDARD DEVIATION OF PERCENTAGE REPAIRED PER BODY $\sigma_X$	STANDARD DEVIATION OF MEAN PER BODY $\sigma_M$
A <sub>1</sub>	2,180	46.2	22.3	30	45.3	24.8	4.6
A <sub>2</sub>	505	7.0	10.3	6	10.4	11.5	5.1
B	164	23.3	15.1	4	23.6	15.3	8.8
Bc <sub>1</sub>	2,231	34.1	19.6	41	29.9	24.8	3.9
Bc <sub>2</sub>	3,101	18.4	19.3	15	13.7	35.0	9.4
C	1,324	13.3	11.0	19	11.8	9.8	2.3
Ca	1,891	6.2	7.5	14	6.1	8.5	2.4
Ch	907	31.7	24.2	20	28.5	23.9	5.5
Ci	562	59.6	25.0	7	45.8	29.5	12.0
Cs <sub>1</sub>	1,659	30.8	16.9	34	29.4	21.9	3.8
Cs <sub>2</sub>	330	3.5	4.8	4	6.4	8.8	5.1
D	317	19.6	28.3	9	22.8	26.6	9.4
E	655	16.1	14.7	15	15.7	14.4	3.8
G	367	33.9	28.9	13	40.3	33.7	9.7
H	928	27.7	15.1	17	38.5	25.6	6.4
K	160	28.6	37.4	4	39.5	43.1	24.9
Kc	745	7.1	5.9	8	7.1	3.3	1.2
L	290	3.3	10.5	5	12.7	22.3	11.1
Li	680	11.1	2.7	3	11.4	2.4	1.7
Lf	184	0.0	....	2	0.0	....	....
M	5,637	20.9	13.3	27	21.7	18.6	3.6
Ms	1,671	22.8	30.6	24	26.6	31.9	6.6
Mu	134	39.4	16.2	3	25.7	21.4	15.2
N	535	57.0	....	2	79.0	....	....
Nf	207	6.5	10.7	6	6.1	10.7	4.8
P	1,160	3.1	5.1	19	3.3	4.9	1.2
S	3,555	4.0	4.2	9	3.7	4.5	1.6
T	610	20.0	20.0	21	22.6	20.9	4.7
Ti	365	26.3	23.0	11	24.5	25.7	8.1
V	4,105	13.6	14.2	35	16.4	16.0	2.7
VI	405	7.1	3.2	4	7.2	4.3	2.5
Wf	278	12.4	8.2	4	12.5	9.1	5.3
WI	3,715	6.0	7.7	39	11.9	14.0	2.3
W	240	6.3	....	1	6.3	....	....
Wa	640	61.0	23.1	5	51.3	24.0	12.0

It is easily seen that the repairs of 570 feet in the 1,000-foot length of pipe line are inconsistent with the fact that only 380 feet of pipe were repaired in the remaining length of 28,000 feet. At the place where the pipe was repaired,

which extended for 200 feet (5 lines) it would appear either that the soil is not really Lordstown sandy loam or the pipe did not require reconditioning solely on account of soil corrosion.

The distribution of corroded areas as related to soil type is shown graphically in figure 1 for a typical section of the lines. Pertinent data such as the total and repaired lengths of line in each area and acidity and resistivity data are also shown.

The marked differences in the corrosiveness of several soil types is immediately apparent in figure 1. In the areas occupied by the Chenango silt loam (D) and the Holly clay loam (H), it is seen that as many as three separate repairs have been made on short lengths of the lines. In contrast to these severely corrosive areas are intervening areas of Wooster loam (W1) in which the repairs have been negligible. Similarly, it is seen that the area occupied by the Mahoning silt loam (M) is corrosive, but that few if any repairs have been made in the Canfield (Ca) and Ellsworth (E) silt loams and in the Volusia loam (V1).

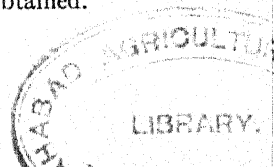
TABLE 3  
*Repair data for Lordstown sandy loam*

LENGTH	REPAIRED LENGTH	PERCENTAGE REPAIRED
<i>feet</i>	<i>feet</i>	
2,000	0	0
1,000	570	57
10,500	0	0
9,500	0	0
6,000	380	6.33
Totals... 29,000	950	3.27

Figure 1 further illustrates the errors, previously referred to, which may occur at the boundaries of the different soils. Thus it is seen that practically all of the repairs which have been necessary in the area of Wooster loam between 1,000 and 5,000 feet have been made at the boundaries of the adjacent soil types.

#### INFLUENCE OF TOTAL ACIDITY AND RESISTIVITY ON CORROSIVENESS OF SOIL TYPES

In view of the importance of soil acidity as a factor in corrosion it was anticipated at the beginning of this study that the average total acidity of the soil types could be correlated with their corrosiveness. Although such a correlation can be shown to hold for certain sections of the line where other factors such as resistivity and topography are subject to only slight variation, no worthwhile correlation between acidity and corrosion obtains for the pipe line as a whole. It can be shown, however, that if the average resistivity of the types is also considered, a fairly satisfactory correlation is obtained.



Distance along lines - thousands of feet.																							
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Repairs-Line No. 1	535 1771 1037				124 447 24	1101 344 44	1101 344 44			1057 344 44		1057 344 44			962 344 44		962 344 44			2752 344 44	1534 344 44		
Repairs-Line No. 2	242 473 24	242 473 24	242 473 24				1101 344 44	1101 344 44	1101 344 44	1101 344 44				1057 344 44	1057 344 44	1057 344 44	1057 344 44	1057 344 44	1057 344 44	1057 344 44	1057 344 44	1057 344 44	1057 344 44
Repairs-Line No. 3	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24
Repairs-Line No. 4	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24	242 473 24
Soil Types (Symbols defined in Table I)																							
DATA ON REPAIRS	4000'	16,800'	24,800'	16,800'	24,800'	16,800'	24,800'	16,800'	24,800'	16,800'	24,800'	16,800'	24,800'	16,800'	24,800'	16,800'	24,800'	16,800'	24,800'	16,800'	24,800'	16,800'	24,800'
Length of line in each soil zone	3651'	1677'	400'	1572'	1192'	14,400'	1200'	2400'	6900'	2400'	1600'	9200'	2800'	6400'	9600'	5190'	3400'	2400'	175'	5'			
Percentage repaired within 300 feet of sample	41																						
DATA FROM SAMPLES																							
Average acidity (me)																							
Maximum acidity (me)																							
Minimum resistivity (ohm-cm)																							

FIG. 1. TYPICAL SECTION OF PIPE LINES SHOWING REPAIRS AND SOIL DATA



In order to study the separate influence of acidity and resistivity on the corrosiveness of the soil types, soils of different acidities but having nearly equal resistivities were arranged in the order of increasing acidity. It was observed that the corrosiveness of such soils was roughly proportional to their acidity. Similarly, by arranging soils of approximately the same acidity in the order of decreasing resistivity, a rough inverse proportionality between corrosiveness and resistivity can be shown. These correlations are illustrated in table 4. In preparing this table the data for the Lorain fine sandy loam was omitted, the extent of the soil along the line (less than one-half mile) being too small to render the data significant.

TABLE 4  
*Repairs in soil types as influenced by total acidity and resistivity*

TOTAL ACIDITY 15-18 M.E.			RESISTIVITY 4000-5000 OHM-CM.		
Soil type	Resistivity	Repairs	Soil type	Total acidity	Repairs
	ohm-cm.	per cent		m.e.	per cent
Lordstown fine sandy loam. . . . .	11,450	3.3	Wauseon fine sandy loam. . . . .	7.5	6.3
Wooster loam. . . . .	8,002	6.0	Caneada silt loam*. . . . .	12.7	13.3
Volusia silt loam. . . . .	5,473	13.6	Miami silt loam†. . . . .	16.8	22.8
Mahoning silt loam. . . . .	4,903	20.9	Mahoning silt loam. . . . .	18.1	20.9
Miami silt loam. . . . .	3,982	22.8	Trumbull clay loam‡. . . . .	21.1	20.0
Nappanee clay loam. . . . .	1,009	57.0	Crosby silt loam, 1st section. . .	22.0	30.8

\* Includes fine sandy loam.

† Includes clay loam and fine sandy loam.

‡ Includes silt loam.

The percentage of the line repaired in the soil types investigated for the particular period may be roughly expressed in terms of the acidity and resistivity of a soil by the equation:

$$P = \frac{7,500 (A - 5)}{R}$$

where  $P$  = the percentage of pipe repaired in each soil type

$A$  = the average acidity of the soil

$R$  = the average resistivity of the soil.

By means of this relation the corrosiveness of each soil type was calculated and the results obtained were plotted against the actual repairs made in the corresponding soils, with the results shown in figure 2.

If only those soils having a wide distribution along the pipe line are considered, it is apparent that the calculated repairs in the majority of these soils are nearly equal to the actual repairs. A possible explanation, which has been



COMPARISON OF CORROSIVENESS OF SOIL TYPES WITH DEGREE OF DEVELOPMENT  
OF THE SOIL PROFILE

In considering further the relation between the various soils and their corrosiveness, it is of interest to compare the repairs made in certain soils with the degree of development of the horizons within the soil profile. In table 5 the typical upland soils of northeastern Ohio, which have developed from sandstone and shale, have been grouped in four vertical columns according to the degree of development shown by their profiles. Within each vertical column the soils are arranged according to the texture of the B-horizon. In table 6 a similar arrangement is shown for the glacial soils of northwestern Ohio, which have been derived from limestone.

It is seen from the tables that the corrosiveness of the soils is related to their stage of development, the less well developed soils being invariably the most corrosive. Thus the Trumbull soils, which are mottled throughout the profile and show very little differentiation into horizons, are seen to be corrosive, whereas the Wooster soils, which are well developed, are non-corrosive. It will also be observed that within the vertical columns corrosiveness increases as the subsoil becomes heavier in texture.

These relations between the stage of development and texture of the soils and their corrosiveness can be largely explained on the basis of their average acidity and resistivity. Because of the slight weathering that has occurred in the case of the poorly developed soils, such as those of the Trumbull series, there has been but little tendency for soluble materials to be removed, with the result that the average resistivity of these soils is relatively low. Similarly, the very heavy texture of poorly drained soils accounts largely for their high acidity, the acidity of a soil being a function of its content of colloidal material. Conversely, the high stage of development of the non-corrosive Wooster soils has resulted from the thorough removal of soluble salts, as indicated by their high average resistivity.

Aside from the effects of acidity and resistivity, however, it is highly probable that those differences in the physical characteristics of the soils which determine their drainage and aeration have an important bearing on the observed relations.

Although it is evident that there is a wide range of variation within the soil type, and that the corrosiveness of a soil type can be only roughly predicted, the economic value of the methods described in combatting corrosion on pipe lines can be abundantly justified. If adequate protection were applied to the pipe lines considered in this study in only those soils which have been shown to be corrosive, very large savings in the annual cost of maintenance could be effected. Ewing (5) in a previous paper has estimated this saving to be 24 per cent of the annual operating cost, using reasonable values for coating and repair costs. It is of course impossible with present methods to determine the corrosiveness of soils accurately, but Ewing has shown that the savings which might be effected by using the formula which connects the repairs in each type

TABLE 5  
*Relation between the degree of development of the glacial soils of northeastern Ohio and their corrosiveness*

	DEGREE OF DEVELOPMENT							
	1		2		3		4	
	Series	Repairs per cent	Series	Repairs per cent	Series	Repairs per cent	Series	Repairs per cent
Color of surface soil.....	Gray		Gray brown		Light brown		Brown	
Mottling of A horizon.....	Mottled		Mottled		No mottling		No mottling	
Mottling of B horizon.....	Mottled		Mottled		Mottled		No mottling	
Mottling of C horizon.....	Mottled						No mottling	
Distinguishing characteristics of B-horizon	Series	Repairs per cent	Series	Repairs per cent	Series	Repairs per cent	Series	Repairs per cent
Light.....	.....	....	Volusia	13.6	Canfield	6.2	Wooster	6.0
Heavy.....	Trumbull	20.0	Medina	*	Rittman	*	.....	....
Very heavy.....	Trumbull	....	Mahoning	20.9	Ellsworth	16.1	.....	....

\* Series not identified along pipe line.

TABLE 6  
*Relation between the degree of development of the glacial soils of northwestern Ohio and their corrosiveness*

	DEGREE OF DEVELOPMENT							
	1		2		3		4	
	Series	Repairs per cent	Series	Repairs per cent	Series	Repairs per cent	Series	Repairs per cent
Color of surface soil.....	Grayish black		Dark gray		Gray brown		Brown	
Color of subsoil.....	Mottled bluish gray		Mottled bluish gray and yellowish brown		Mottled yellowish brown and yellowish gray		Reddish brown no mottling	
Distinguishing characteristics of B-horizon	Series	Repairs per cent	Series	Repairs per cent	Series	Repairs per cent	Series	Repairs per cent
Light.....	.....	....	.....	....	Miami	22.8	Bellefontaine	*
Heavy.....	Clyde	46.2	Brookston	34.1	Crosby	30.8	.....	....
Very heavy.....	.....	....	Paulding	*	Nappanee	57.0	.....	....

\* Series not identified along pipe line.

with the average acidity and resistivity, may amount to about 16 per cent of the annual maintenance cost.

#### SUMMARY

The soils occurring along a 200-mile section of a pipe line system in Ohio have been mapped, and the corrosiveness of each type has been estimated from the corrosion actually experienced in operating the pipe lines. The average total acidity and resistivity of each of the soil types were determined and correlated with the known corrosiveness of the soils. A formula was derived whereby the corrosiveness of the soils can be approximated from the values for total acidity and resistivity. Flood plain and terrace soils are, however, more corrosive than would be indicated by the formula. The corrosiveness of the soils has been related to the texture of the subsoil and to the degree of development shown by the soil profile. Soils having the heaviest subsoils and showing the least profile development were found to be the most corrosive. Very little corrosion occurred in light-textured, well-drained soils.

#### REFERENCES

- (1) DENISON, I. A. 1931 Correlation of certain soil characteristics with pipe line corrosion. *Bur. Standards Jour. Res.* 7: 631.
- (2) DENISON, I. A. 1933 Methods for determining the total acidity of soils. *Bur. Standards Jour. Res.* 10: 413.
- (3) DENISON, I. A., AND HOBBS, R. B. 1934 Corrosion of ferrous metals in acid soils. *Bur. Standards Jour. Res.* 13: 125.
- (4) EWING, S. P. 1931 Field study of a long gas line. *Amer. Gas. Assoc. Mo.* 13: 70-76.
- (5) EWING, S. P. 1934 Corrosion surveys for transmission lines and distribution systems. *Proc. Amer. Gas. Assoc.* 1934: 846.
- (6) SHEPARD, E. R. 1931 Pipe line currents and resistivity as indicators of local corrosive soil areas. *Bur. Standards Jour. Res.* 6: 683.



# A COMPARISON OF POTASSIUM PERMANGANATE AND CERIC SULFATE FOR THE OXIDATION OF COBALTINITRITE IN THE ESTIMATION OF POTASSIUM IN KCl SOLUTION AND IN AMMONIUM ACETATE SOIL-EXTRACTS<sup>1</sup>

HENRY C. HARRIS<sup>2</sup>

*Delaware Agricultural Experiment Station*

Received for publication December 15, 1934

The studies reported herein grew out of experimentation in connection with another problem in which it was desired to determine the replaceable potash in a number of field plots located on Sassafra silt loam soil. Neutral normal ammonium acetate was used to extract the soil. The extract was evaporated to dryness over a steam bath, and the organic matter was destroyed by twice adding and evaporating aqua regia over a steam bath and then removing the silica by double dehydration. The potash was then determined by means of platonic chloride according to the Official Method (1) for the determination of potash in mixed fertilizers. Since the small amount of potash in the extract necessitated the use of practically all of one leachate for a single determination, and since duplicate determinations frequently disagreed, the use of the platonic chloride method was discontinued and the sodium cobaltinitrite method tried.

Most of the workers using the sodium cobaltinitrite method, including Milne (3), Hibbard and Stout (2), and Volk and Truog (5) add an excess of potassium permanganate and a small amount of sulfuric acid to the precipitate and bring to a boil. Then an excess of either standard oxalic acid or sodium oxalate is added and titrated to a faint pink with potassium permanganate. Schueler and Thomas (4), however, titrate directly with permanganate without the uses of an oxalate solution. They claim the direct titration is much quicker and just as accurate. For that reason it was decided to try their modification of the sodium cobaltinitrite method.

## PRELIMINARY EXPERIMENTS

A stock solution of KCl in water was prepared for use in some preliminary experiments so that 10 cc. of the solution would contain 5.244 mgm. of potassium. Determinations by the Schueler and Thomas method were made on a number of 10-cc. aliquots of the solution. At first the results were all low, probably because of the loss of nitrous acid during titration. Later, satisfac-

<sup>1</sup> Published with the permission of the director of the Delaware Agricultural Experiment Station. Contribution from the department of agronomy.

<sup>2</sup> Assistant professor of agronomy.



tory results were obtained by keeping an excess of the permanganate in the upper part of the liquid while titrating until the end point was approached. It takes a little practice to learn how to do this titration. Gently stir the top of the liquid in the beaker with a glass rod, but do not stir the whole contents of the beaker until the titration is almost completed.

Five determinations were made on the stock solution using the Schueler and Thomas method up to the point of titration. At that point excess permanganate and 10 cc. of 1:1 sulfuric acid were added and brought to a boil; excess standard sodium oxalate was added and then titrated to a faint pink with permanganate. The results were essentially the same as those from direct titration with permanganate. This supports the contention that the use of an oxalate is not necessary.

Schueler and Thomas prescribe a wash solution. In several determinations ice-cold distilled water was compared with the wash solution. There was very little difference in the results: the water apparently gave slightly lower values. Probably the cold water would be satisfactory, provided the proper factor were used.

Some workers do not use alcohol in connection with the cobaltinitrite method. For that reason four determinations were made on the stock solution by the Schueler and Thomas method, except that no alcohol was added. If the factor given by those authors is used in calculating the potassium values, the results were all low. However, the potassium equivalent factor for these four determinations was calculated and found to correspond almost exactly to the one given by Volk and Truog (5), who use no alcohol in this connection. This seems to indicate that alcohol can be used or left out depending on what factor is used.

The asbestos pad recommended for filtering does not always work well. It may be too thick or too compact for rapid filtering. When the pad is thick, considerable washing may be necessary to remove the excess cobaltinitrite solution. Besides, this asbestos pulp in the titration beaker interferes to some extent in determining the exact end point. These objections to the asbestos pad led the author to try talc in a Jena fritted glass filter funnel 39 G 3.<sup>3</sup> This method was found more satisfactory. When the talc is properly prepared and correctly placed in the funnel the filtration is rapid, less washing is required, and the small amount of talc transferred to the titration beaker interferes less in determining the exact end point. The talc has to be thoroughly washed and the finer particles removed by decantation. A water suspension of the washed product should be prepared of such a consistency that a few cubic centimeters when poured in the fritted glass filter funnel and allowed to settle will form a talc layer somewhat thinner than 1 mm. The talc suspension should be

<sup>3</sup> Since this paper was submitted for publication a Jena fritted glass filter funnel 39G2 has been specially imported. In connection with the talc, it filters much more rapidly than the 39G3 funnel, and the results obtained seem to be just as reliable. Of several fritted glass filters tried, the author prefers for this particular determination the 39G2.



allowed to settle for about one-half minute, and then strong suction used to remove the surplus water. It is then ready for filtration. The talc layer should be firm and should not allow any of the precipitate to go through and collect on the fritted glass. The fact that the suspension is measured enables one to prepare a filtering surface essentially alike every time.

In removing the precipitate the funnel can be tilted to such an angle that a few cubic centimeters of cold distilled water sprayed inside the funnel will wash all of the precipitate and talc into the titration beaker. To make certain that no precipitate is left adhering to the funnel a stream of boiling water is sprayed inside the funnel and allowed to run down its side into the titration beaker. About 150 cc. of the boiling water is used for this purpose, bringing the temperature of the solution to a point where immediate titration can be made.

The fritted glass funnel after use can be quickly cleaned by drawing water through it in the opposite direction.

These preliminary experiments on the KCl solution made modifications of the Schueler and Thomas method seem unnecessary. For that reason the original method was tried on the ammonium acetate soil-extracts. The only modification ever made was that of filtration, which has been described.

#### DUPLICATION OF RESULTS ON AMMONIUM ACETATE SOIL-EXTRACTS

The method of extracting the soil and the procedure used in the determinations were as follows: The equivalent of 100 gm. of dry soil was leached with 750 cc. of neutral normal ammonium acetate. An aliquot was evaporated to dryness in a beaker on a steam bath, the sides of the beaker were washed down with water, 10 cc. of aqua regia was added and brought to dryness, again the sides of the beaker were washed down, and 5 cc. of aqua regia was added and brought to dryness. Then the beaker was flamed in a free flame to drive off the ammonium chloride which will adhere to the beaker. Care was taken not to get the beaker hot enough to drive off any of the potassium salts. After this, the residue of salts was brought into solution with distilled water and a few drops of HCl. From that point the Schueler and Thomas method was followed.

Repeated determinations of the potassium in ammonium acetate extracts of the same soil sample from a limed and an unlimed plat located on Sassafras silt loam were made. The repetitions were done at different times extending over a period of about two months. The results, given in table 1, indicate that on this kind of soil the method will give essentially the same result every time. Furthermore, known amounts of potassium added to the leachates were recovered by this method reasonably well. That gives an additional indication of reliability for use in this connection. The results thus obtained justified the determination, by the method described, of the potash in the ammonium acetate extract of a number of soil samples taken from field plats on Sassafras silt loam soil, the results of which will not be given here.

## POSSIBLE OBJECTIONS TO POTASSIUM PERMANGANATE

Experience with these determinations indicated the possibility of two objections to potassium permanganate as used in the Schueler and Thomas method.

One is that the end point is not always sufficiently sharp. In these experiments 0.05 *N* permanganate was used, and the addition of three or four drops at the end point sometimes made little difference in color. This was particu-

TABLE 1

*Results of repeated determinations, by the cobaltinitrite method, of the potassium in ammonium acetate leachates of the same Sassafras silt loam soil from block B*

PLAT	LEACHATE	ALIQOT TAKEN FOR DETERM- INATION	K ADDED TO ALIQOT	K FOUND	ADDED K RECOV- ERED	K PER 100 GM. DRY SOIL	AVERAGE
		cc.	mgm.	mgm.	mgm.	mgm.	mgm.
4 unlimed	Diluted to 1,000 cc. with H <sub>2</sub> O	200		0.85		4.25	4.18
		200		0.82		4.10	
4 unlimed	Diluted to 1,000 cc. with H <sub>2</sub> O	200		0.82		4.10	4.00
		200		0.78		3.90	
4 unlimed	Not diluted	200		1.27		4.36	4.21
		200		1.18		4.05	
		200	5.24	6.19	4.96		
4 unlimed	Not diluted	200		1.12		3.79	3.99
		200		1.24		4.19	
		200	5.24	6.25	5.07		
4 limed	Not diluted	275		2.00		4.28	4.28
4 limed	Not diluted	275		1.99		4.28	4.28
4 limed	Not diluted	200		1.33		4.57	4.36
		200		1.21		4.16	
		200	5.24	6.33	5.06		
4 limed	Not diluted	200		1.27		4.34	4.29
		200		1.24		4.24	
		200	5.24	6.51	5.25		

larly true in the presence of the asbestos pad. The talc did not seem to interfere as much as the asbestos.

In order to prevent the loss of nitrous acid during titration it is desirable to keep an excess of permanganate in the upper part of the liquid in the titration beaker until the end point is almost reached. The second objection is that in attempting to keep this excess one sometimes runs past the end point.

These considerations suggested the use of some other substance to oxidize

the cobaltinitrite. The fact that ceric sulfate is known to be a good oxidizing agent, and that Professor C. C. Lynch, Chemistry Department of the University of Delaware, has been using it in some of his work on potash determinations, led to its trial in this connection.

#### PRELIMINARY TESTS AND CERIC SULFATE METHOD

A 0.05 *N* solution of ceric sulfate was prepared and standardized. After the solution had stood in the laboratory in an ordinary glass-stoppered bottle for three months the standardization was repeated and found to be the same as at first. This indicates that the solution is very stable.

Ferrous ammonium sulfate, with ortho-phenanthroline ferrous complex as an indicator, was selected for titrating excess ceric sulfate. A trial of the titration was made with solutions at room temperature. The end point was very sharp. Less than one drop of a 0.05 *N* solution will give a change in color from a pale blue to a deep orange-red. The color contrast is so great that the author was able to titrate at night without special lights. Repeated trials always gave the same result.

The titration was repeated with hot solutions, but the results were not so good. The indicator does not appear to be very stable in hot solutions.

The preliminary tests led to the adoption of the same procedure for ceric sulfate as that used in connection with permanganate up to the point where the hot solution is in the titration beaker. At that point an excess of ceric sulfate is run down the side of the beaker by means of a pipette, the solution stirred, 10 cc. of 1:1  $\text{H}_2\text{SO}_4$  added in the same manner, the solution again stirred, and the beaker put in a pan of water to cool. After the solution has reached room temperature the excess ceric sulfate is titrated with ferrous ammonium sulfate, one drop of ortho-phenanthroline ferrous complex being used as an indicator.

#### POTASSIUM EQUIVALENT FACTORS FOR PERMANGANATE AND CERIC SULFATE

Potassium determinations by the Schueler and Thomas and by the ceric sulfate methods were made on 10-cc. aliquots of the stock KCl solution already described. They were done at different times over a period of about a month. In all, seventeen determinations were made with potassium permanganate and sixteen with ceric sulfate. The results were used to calculate the potassium equivalent of 1 cc. of 0.1 *N* solution. The average for the permanganate determinations was 0.0005553 gm. of potassium. The largest factor for the individual determinations was 0.0005834 gm. of potassium, and the smallest, 0.0005406. Most of them were very near the average. For the ceric sulfate determinations the average was 0.0005616, the largest was 0.0005797, and the smallest was 0.0005497 gm. of potassium. Thus it can be seen that the potassium equivalent factor for ceric sulfate is essentially the same as that for potassium permanganate and the ones obtained here are very close to 0.0005672, the factor given by Schueler and Thomas.

## COMPARISONS ON SOIL EXTRACTS

As already indicated, the potassium permanganate method seems to be very reliable for the determination of potassium in the ammonium acetate extract of Sassafras silt loam soil. In order to compare the potassium permanganate and ceric sulfate methods on the same soil extract, another sample of Sassafras silt loam was obtained and leached as before. Four aliquots of the leachate were taken. On two of the aliquots potassium determinations were made by

TABLE 2

*Comparison of potassium determinations on the same ammonium acetate leachate of sassafras silt loam soil*

150-cc. aliquot taken for each determination

NUMBER	METHOD USED	K FOUND	K PER 100 GM. SOIL
		mgm.	mgm.
1	KMnO <sub>4</sub>	0.79	3.54
2	KMnO <sub>4</sub>	0.76	3.41
3	Ceric sulfate	0.77	3.46
4	Ceric sulfate	0.77	3.46

TABLE 3

*Comparison of potassium determinations on the same ammonium acetate leachate of Chester loam soil*

150-cc. aliquot taken for each determination

SAMPLE	TREATMENT OF SAMPLE BEFORE LEACHING	DETERMINATION	METHOD	K IN ALIQUOT	K PER 94 GM. SOIL
				mgm.	mgm.
1		1	Ceric sulfate	3.79	17.18
		2	Ceric sulfate	3.74	16.93
		3	KMnO <sub>4</sub>	3.71	16.80
		4	KMnO <sub>4</sub>	3.71	16.80
2	10.488 mgm. K added	1	Ceric sulfate	5.97	26.60
		2	Ceric sulfate	5.89	27.22
		3	KMnO <sub>4</sub>	5.95	27.48
		4	KMnO <sub>4</sub>	5.95	27.48

the potassium permanganate method as previously used on this soil. On the other two, the procedure used in connection with the potassium permanganate method was followed up to the point of titration. From that point on the procedure given for the ceric sulfate method was followed. The results are given in table 2. An examination of the data indicates that the two methods of procedure give practically the same results.

The two methods were also compared on Chester loam soil. Samples equivalent to 94 gm. of dry soil were taken. One sample was leached in the way

already described. To another sample 20 cc. of KCl solution containing 10.488 mgm. of potassium was added, and then the soil was immediately leached in the regular way. Potassium was determined by the two methods. The results are given in table 3. Again the results by the two methods are very similar.

It was desired to compare further the two methods on a very sandy soil. Norfolk sand, which is known to be very low in replaceable potassium, was selected. To obviate the taking of a small aliquot in making a number of determinations on the same leachate, 225 gm. of air-dried soil was leached with 1,688 cc. of the neutral normal ammonium acetate. The proportion of soil to the acetate is the same as that used in the other leachings. Potassium determinations were made by the two methods, and the results are given in table 4.

TABLE 4

*Comparison of potassium determinations on the same ammonium acetate leachate of Norfolk sand*  
200-cc. aliquot taken for each determination

DETERMINATION	METHOD	K ADDED TO ALIQUOT	K FOUND	ADDED K RECOVERED	K PER 100 GM. SOIL
		mgm.	mgm.	mgm.	mgm.
1	KMnO <sub>4</sub>		0.52		1.85
2	KMnO <sub>4</sub>		0.49		1.74
3	Ceric sulfate		0.50		1.77
4	Ceric sulfate		0.52		1.86
5	KMnO <sub>4</sub>	5.24	5.92	5.41	
6	KMnO <sub>4</sub>	5.24	5.92	5.41	
7	Ceric sulfate	5.24	6.01	5.50	
8	Ceric sulfate	5.24	5.96	5.45	

The determinations on Norfolk sand by the two methods agree almost perfectly. Potassium added to the leachate was recovered, with a slight excess, approximately 0.2 mgm., by both methods. In dealing with such small amounts of potassium some error is to be expected.

#### DISCUSSION

Tests made on the ammonium acetate extracts of Sassafras silt loam, Chester loam, and Norfolk sand indicate that ceric sulfate in connection with sodium cobaltinitrite can be used for the determination of potassium in that extract with about the same degree of accuracy as with potassium permanganate. Schueler and Thomas claim that their method is most accurate when determining amounts of potassium between 3 and 10 mgm. Sassafras silt loam and Norfolk sand are so low in replaceable potassium that it was not possible to repeat as often as desired the determinations on the same leachate and take an aliquot sufficiently large to be in the aforementioned range. Nevertheless, on the basis of the recovery of known amounts of potassium added to some of the aliquots, the determinations on those two soils are thought to be reasonably

accurate. Chester loam contains much more replaceable potassium, and the aliquots were within the prescribed range.

The end point with ceric sulfate, when othro-phenanthroline ferrous complex is used as an indicator, is sharper with a greater contrast of color than the end point with permanganate. However, factors other than the end point apparently limit the accuracy of the methods because the sharper end point of the ceric sulfate made no appreciable difference in the results. Nevertheless, if the other limiting factors could be removed the sharp end point of the ceric sulfate would be an advantage. The author prefers to deal with a sharp end point with contrasting colors even though the results are the same.

The Schueler and Thomas method, where the titration is made directly with potassium permanganate, may be more rapid than the ceric sulfate method. The author is not certain that such is the case, however, because a standardized pipette can be used to put the excess ceric sulfate into the titration beaker, and this takes little time. Then the only titration which has to be done is the excess ceric sulfate with ferrous ammonium sulfate. Waiting for the solutions to cool before titration involves no loss of time because a number of determinations are most frequently done at the same time. Some can be prepared while others are cooling. In titrating directly with permanganate, in his efforts to keep an excess of permanganate in the titration beaker till the end point is approached one may occasionally go beyond the end point, which is never the case in the ceric sulfate method. Because of that fact, the ceric sulfate method, even though it might be a little less rapid, is perhaps preferable to the Schueler and Thomas method.

In those methods which require two titrations with permanganate and one with an oxalate it seems to the author that the use of the ceric sulfate in place of the potassium permanganate should have considerable advantages.

#### SUMMARY AND CONCLUSIONS

Preliminary experiments in connection with the Schueler and Thomas method indicated that there is a possibility of using ice-cold distilled water for the wash solution. Alcohol may not be necessary. Talc with a fritted glass funnel seemed to be better for filtration than an asbestos pad.

The Schueler and Thomas method is reliable for the determination of potassium in the ammonium acetate leachate of Sassafras silt loam soil, if duplication of results and the recovery of potassium added to the leachate are considered measures of reliability.

A procedure for the determination of potassium by means of ceric sulfate is given.

A comparison between seventeen determinations of potassium in a KCl solution by means of potassium permanganate and sixteen determinations on the same solution by means of ceric sulfate was made. The potassium equivalent factors were essentially the same.

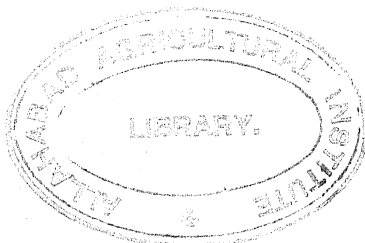
The ammonium acetate extracts of Sassafras silt loam, Chester loam, and

Norfolk sand were analyzed for potassium by both methods. There was close agreement in all cases. Known amounts of potassium added to some of the leachates were recovered reasonably well, indicating that both methods are reliable for the determination of small amounts of potassium in these soil extracts.

In some respects ceric sulfate seems to be preferable to potassium permanganate for potassium determinations.

#### REFERENCES

- (1) Association of Official Agricultural Chemists. 1930 Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists. Washington, D. C.
- (2) HIBBARD, P. L., AND STOUT, P. R. 1933 Estimation of potassium by titration of the cobaltinitrite with potassium permanganate. *Jour. Assoc. Off. Agr. Chem.* 16: 137-140.
- (3) MILNE, G. 1929 The cobaltinitrite (volumetric) method of estimating potassium in soil-extracts. *Jour. Agr. Sci.* 19: 541-552.
- (4) SCHUELER, J. E., AND THOMAS, R. P. 1933 Determination of potassium by sodium cobaltinitrite. *Indus. and Engin. Chem. (Anal. Ed.)* 5: 163-165.
- (5) VOLK, N. J., AND TRUOG, E. 1934 A rapid chemical method for determining the readily available potash of soils. *Jour. Amer. Soc. Agron.* 26: 537-546.







# ORGANIC SOIL CARBON BY REDUCTION OF CHROMIC ACID<sup>1</sup>

L. E. ALLISON<sup>2</sup>

*Illinois Agricultural Experiment Station*

Received for publication January 2, 1935

A study of the organic carbon content of soils involves two pertinent considerations; namely, representative sampling and the use of suitable analytical methods. It is recognized that, because of the non-uniform nature of soils even within short distances, sampling errors usually exceed analytical errors. Soil carbon is no exception. In order to reduce the sampling error equal to, or below, the error of analysis a larger number of individual borings is necessary than is ordinarily taken. With 20 borings per twentieth-acre plot, a difference of from 3 to 5 per cent between duplicate samples frequently occurs, which is reduced only very slightly by further increase in the number of borings per plot. There is little justification, therefore, for attaining, at the expense of much time, a degree of accuracy in analysis far in excess of that which is attained in sampling.

Two methods are commonly used for carbon determinations, both of which offer certain disadvantages. Wet combustion (4, 10) is time-consuming and, moreover, is subject to the danger involved in handling boiling sulfuric acid. Standard furnace combustion (11) (combustion in a tube furnace with current of oxygen, purifying train, and absorbant in bulb for gravimetric estimation of CO<sub>2</sub>) is more accurate than the former for determining total soil carbon, but it is also slow and requires expensive apparatus. This method does not distinguish between organic- and carbonate-carbon and is subject to the additional objection, particularly where agronomic interpretations are involved, of determining inert carbon, derived from cinders, fragments of coal, or carbonized soil organic matter. From the standpoint of soil productivity this inert carbonaceous matter does not function in the same manner as organic matter derived from decaying vegetation.

Recently Anderson and Byers (1) pointed out the need for a method capable of "distinguishing between charcoal and coal fragments and soil organic matter." An experience of the writer bears upon this question. In checking Schollenberger's chromic acid reduction method (5, 6) against standard furnace combustion (11) on some laboratory stock samples, widely divergent carbon

<sup>1</sup> Contribution from the Division of Soil Biology, department of agronomy, Illinois Agricultural Experiment Station, Urbana, Illinois. Published with the approval of the director of the station.

<sup>2</sup> Assistant in soil biology.

values were obtained for sample 14043. Furnace combustion gave values 21 per cent higher than the reduction method (table 1). After the analysis was repeated with similar results the source of the sample was investigated. This sample was obtained within a few feet of a railroad right-of-way and, upon physical analysis, revealed the presence of fragments of cinders and incompletely burned coal. Sample 14052 taken 200 feet farther from the railroad was cinder-free, and its carbon value showed good agreement by the two methods. These data suggest that the chromic acid reduction procedure, by failing to determine relatively inert carbon, gives data more nearly representing the organic carbon of the soil than does the furnace combustion method.

Since both the wet and dry combustion methods for determining organic carbon have objectionable features, the writer directed his attention to Schollenberger's chromic acid reduction method (5, 6). In addition to being rapid, it requires only simple apparatus. This paper reports a study of the value of the method for the determination of soil organic carbon.

TABLE 1

*Effect of inert carbon on percentage of total soil carbon by two different methods*

SAMPLE*	LOCATION	INERT CARBON	CARBON	
			Furnace combustion	Chromic acid reduction
			<i>per cent</i>	<i>per cent</i>
14043	Near railroad	Cinders	2.36	1.95
14052	200 feet from railroad	None	2.27	2.24

\* Samples from S. W. 1/4 of Sec. 15, T. 15 N., R. 6 W. of 3rd P. M. in Sangamon County, Illinois.

The method, in brief, consists in the oxidation of a sample in concentrated sulfuric acid containing excess potassium dichromate, by heating to 175°C. in 90 seconds, cooling, and titrating the *unused* chromic acid with a standard solution of 0.2 *N* ferrous ammonium sulfate, using diphenylamine as internal indicator.

#### EXPERIMENTAL

As stated by Schollenberger (5), 1 ml. of 0.2 *N* ferrous ammonium sulfate is equivalent to 0.009807 gm. of potassium dichromate or 0.0006 gm. of carbon. Based on a uniform sample of 0.5000 gm. and 100 per cent recovery, the theoretical factor for carbon is, then:  $0.0006 \times 100/0.5 = 0.12$  per cent for each milliliter of ferrous ammonium sulfate. By the use of this value with furnace combustion as a standard of comparison, the percentage recovery on five 100-mesh, carbonate-free samples, representing surface and subsoil as well as different soil types, was found to vary between 86.1 and 87.8 per cent, averaging 86.9 per cent (column 5, table 2). These results indicate a uniformly incomplete oxidation of organic carbon. A conversion factor equivalent to 100 per

cent recovery of carbon was obtained as follows:  $100 / 86.9 = 1.15$ . By combining this with the theoretical factor as modified for a 0.5 gm. sample, a single factor is obtained for computation: thus, 1 ml. of ferrous ammonium sulfate =  $1.15 \times 0.12 = 0.138$  per cent organic carbon. Further evidence of the correctness of this factor is presented later.

Nearly all investigators reporting the use of Schollenberger's method have recommended modifications. In these modifications, however, either the accuracy of the method or the rapidity of its operation has been impaired.

Degtjareff (3) advised the addition of 10–15 ml. of 0.3 per cent  $H_2O_2$  to the sample followed by a 1.6 per cent chromic acid solution in concentrated  $H_2SO_4$ .

TABLE 2  
*Calibration of Schollenberger's chromic acid reduction method against soils of known carbon content*  
Air-dry basis

SAMPLE NUMBER	CARBON BY FURNACE COMBUSTION	CARBON USING THEORETICAL FACTOR: 1 ML. 0.2 N $Fe^{++}$ SOLUTION = 0.12 PER CENT CARBON		CARBON RECOVERY	CARBON USING CALCULATED FACTOR: 1 ML. 0.2 N $Fe^{++}$ SOLUTION = 0.138 PER CENT CARBON
		per cent	Average		
3 777	4.11	3.60 3.62	3.61	87.84	4.15
3 780	1.66	1.43 1.45	1.44	86.75	1.65
K 301	3.31	2.86 2.84	2.85	86.11	3.28
K 308	4.01	3.48 3.50	3.49	87.04	4.01
K 309	3.92	3.39 3.42	3.40	86.74	3.91
Average.....				86.90	

He applied no external heat because the heat of solution of  $H_2SO_4 + H_2O_2$  was considered sufficient to oxidize the sample. All subsequent steps were the same as in the original procedure. The writer found the method inconsistent. A similar finding has recently been reported by Walkley and Black (9). They studied Degtjareff's method in detail including the interaction of  $H_2O_2$  and chromic acid and found that "the procedure is without a sound theoretical basis for its action."

Tiurin (8), who likewise condemned Degtjareff's procedure, recommends boiling the sample for 5 minutes in a solution of chromic acid in 1:1 sulfuric acid and water. In checking this method good agreement was obtained with

Schollenberger's method where the boiling was controlled with a flame. When a hot plate was used the controls failed to boil, but rather evaporated slowly with a rise in temperature, giving low titrations and incurring a considerable error. This method gave no higher recovery of organic carbon and since it requires 5 minutes boiling as contrasted to heating for only 1.5 minutes, it seems to offer no advantage over the original method.

Following their study of the Degtjareff method, Walkley and Black (9) recommended that the method be simplified by adding the chromic acid in aqueous solution to the sample followed by the addition of 20 ml. of concentrated  $\text{H}_2\text{SO}_4$ , allowing the heat of solution of water and acid to replace the application of external heat. After being shaken one minute the sample is cooled and titrated in the usual way. This method was found by the writer to give a maximum temperature of  $124^\circ\text{C}.$ , which is not sufficiently high to recover a definite fraction of organic carbon present in different soils. The percentage recovery reported by Walkley and Black ranged from 60 to 86 per cent.

Following is Schollenberger's method in detail as used in the work reported in this paper. Experience with the method has led the writer to make a few minor changes, which are reported because they offer what seems to be a simplification of the technic, giving some increase in rapidity without sacrificing accuracy.

Reagents:

1. Potassium dichromate, C.P., pulverized and dried.
2. Fifth-normal ferrous ammonium sulfate. Dissolve 78.6 gm. of C.P. crystals in distilled water containing 20 ml. of  $\text{H}_2\text{SO}_4$  and make up to 1 liter. This reagent may be prepared in larger quantities and stored under hydrogen supplied by a Kipp generator. Since deterioration is very slow under hydrogen, controls need be run only every week or 10 days.

3. Indicators:

- a. Diphenylamine—Dissolve 0.5 gm. in 100 ml. of conc.  $\text{H}_2\text{SO}_4$ ; pour carefully into 20 ml. cold water.

- b. Alternate indicators:

Ortho-phenanthroline.

Barium diphenylamine sulfonate.

Procedure: Weigh 0.1961 gm. potassium dichromate and place in a 150 x 25 mm. Pyrex test tube. In order to save the time of individual weighings of the dichromate, add a 10-ml. portion, using a standardized pipette, to each tube from a solution prepared by dissolving 19.61 gm. of the salt in 1 liter of distilled water. Place tubes in wire basket or racks and take down to dryness overnight in an oven at  $80-85^\circ\text{C}.$  Avoid higher temperatures to prevent spattering.

Weigh 0.5000 gm. soil and transfer into tube. Add 10 ml. of conc. sulfuric acid from a burette so as to wash down wall of tube.

Place tube in ring stand fitted with a suitable clamp. Heat steadily over a low flame (2-3 cm. high), while stirring constantly to the bottom of the tube

with a 350° thermometer, so that a temperature of 175°C. is attained in about 90 seconds. Avoid heating above 180° and also avoid heating too rapidly, which causes excessive fuming of acid. Careful attention to these points is essential to success with the method.

Allow tube to cool 5 minutes in air and then in running tap water until thoroughly cooled. Pour contents of tube into 50 ml. of cool distilled water in 250-ml. beaker and rinse tube several times or until total volume is about 150 ml. Add about 5 gm. sodium fluoride—a level teaspoonful.

Titrate with 0.2 *N* ferrous ammonium sulfate. With 3 drops of diphenylamine the color change is from blue to green, giving a slow but distinct transition at the end point. Ortho-phenanthroline and barium diphenylamine sulfonate (7) give instantaneous changes from pale blue to red and from blue to green, respectively, and for that reason offer some advantage over diphenylamine.

Deduct the burette reading from that of a blank determination made under exactly similar conditions, except that no sample is used. If 0.2 *N* ferrous ammonium sulfate is used, the blank titration, against 0.1961 gm. of potassium dichromate, should be exactly 20 ml. In case the solution is more, or less, than 0.2 *N* the corresponding organic carbon factor may be obtained by substituting the blank titration in the following equation:

$$\frac{20.00}{\text{ml. blank}} \times 0.138 = \text{new factor}$$

In comparative studies with this method best results were obtained where a uniform weight of sample (0.5000 gm.) was used. For soils of 2.5 per cent or more of organic carbon it is preferable to use one and one-half or two times the previously designated weight (.1961 gm.) of dichromate rather than to reduce the sample below 0.5000 gm. A moderate excess of dichromate is essential, otherwise a considerable error may occur. As soon as properly cooled, the oxidized samples should be diluted to the required concentration, after which they may be permitted to stand. This permits 10 or more oxidations and subsequent titrations in a single group.

Since the quantity of soil actually used is small, carefully prepared, 100-mesh samples should be used, although for roughly quantitative work whole, unground samples serve satisfactorily. Pulverizing in an iron mill is satisfactory for all soils except those containing considerable sand. In the case of the latter, sufficient iron may be ground off the mill plates to cause appreciable errors, since iron acts to some extent as a reducing agent. For normal agricultural soils, however, this factor is negligible provided the samples are screened free of pebbles or coarser particles.

Since the reduction method has been calibrated against a relatively small number of samples it seemed desirable to subject it to a more extensive test. Fifteen laboratory stock samples<sup>3</sup> of known carbon content by furnace com-

<sup>3</sup> These samples were supplied by Mr. Eric Winters, Jr., of the Division of Soil Physics, who made the chemical analysis by the furnace combustion method (11), the data for which are reported in table 3.

bustion were used. They represent different horizons from four common soil types occurring in Illinois and provide a wide range in carbon content. The analysis of these samples (table 3) indicates that the reduction procedure gives consistent recovery of carbon in all horizons regardless of amounts present. In other words, the organic matter in the different horizons is attacked to the same degree under the conditions of the method.

A study of organic matter accumulation on certain of the outlying soil experiment fields of the Illinois Experiment Station, in progress at the time the method was being studied, offered an opportunity to compare the errors

TABLE 3

*A comparison of Schollenberger's chromic acid reduction method for organic soil carbon with furnace combustion*

Dark-colored soils

NUMBER	TYPE	HORIZON	DEPTH	CARBON	
				Furnace combustion	Chromic acid reduction*
			<i>inches</i>	<i>per cent</i>	<i>per cent</i>
13 777	Muscatine silt loam	A <sub>1</sub>	0-8	4.11	4.18
13 780	Muscatine silt loam	B <sub>1</sub>	18-25	1.66	1.69
14 052	Muscatine silt loam	A <sub>1</sub>	0-8	2.27	2.24
14 034	Muscatine silt loam	A <sub>1</sub>	0-6	2.53	2.49
14 035	Muscatine silt loam	A <sub>2</sub>	8-14	1.46	1.46
14 036	Muscatine silt loam	B <sub>1</sub>	14-18	0.86	0.87
13 873	Grundy silt loam	A <sub>1</sub>	0-6	3.13	3.18
13 876	Grundy silt loam	A <sub>4</sub>	14-17	1.98	1.98
13 878	Grundy silt loam	B <sub>2</sub>	23-27	0.70	0.69
13 915	Tama silt loam	A <sub>1</sub>	0-6	2.38	2.38
13 918	Tama silt loam	B <sub>1</sub>	13-18	1.11	1.08
13 920	Tama silt loam	B <sub>3</sub>	29-35	0.42	0.42
14 075	Putnam silt loam	A <sub>1</sub>	0-6	2.35	2.43
14 076	Putnam silt loam	A <sub>2</sub>	6-12	1.22	1.20
14 078	Putnam silt loam	B <sub>1</sub>	16-22	0.68	0.63

\* Using new factor: 1 ml. 0.2 *N* ferrous ammonium sulfate = 0.138 per cent organic carbon.

involved in sampling with those of analysis, using furnace combustion (11) as the standard of reference.

Fourteen unlimed twentieth-acre plots from the Raleigh field and a similar number from the Ewing field were sampled by taking 20 borings to a depth of 7 inches, according to the following plan:

a	b	a	b	a	b	a	b	a	b
b	a	b	a	b	a	b	a	b	a
a	b	a	b	a	b	a	b	a	b
b	a	b	a	b	a	b	a	b	a

The "a" borings and the "b" borings were composited separately to make the duplicate samples. Thus from each field 14 duplicate samples were obtained. The samples were air-dried and were passed through a Braun pulverizer and then through a 100-mesh sieve.

#### DISCUSSION OF RESULTS

The carbon values for the duplicate samples obtained from the Raleigh and the Ewing fields are given in table 4. An interpretation of these data is given in table 5 in such a manner as to afford a comparison of the errors of sampling and those due to the two different methods of analysis used in this study.

Standard deviations, by Students' method (2), were computed by considering differences between duplicate soil samples as deviations of the carbon value of duplicate "b" from that of duplicate "a", the latter serving as the base for comparison. In a similar way differences between the two chemical methods are reported as deviation of the carbon value by chromic acid reduction from that by furnace combustion, where the latter serves as the base for comparison. Since standard deviations alone do not give direct information concerning either the magnitude or the frequency of occurrence of the individual deviations, for methods of analysis or of sampling, these facts are presented in table 5, along with standard deviations.

The outstanding fact indicated by the data in table 5 is that the variation between chromic acid reduction and furnace combustion (S.D. = 1.18-1.24) is significantly less than the variation between duplicate samples by either method of analysis (S.D. = 1.50 for combustion and 1.90 for reduction). This point is borne out also by the fact that the reduction values deviate from the combustion values by 2 per cent or more of the carbon in the sample in only three instances out of a total of 56, whereas, the "b" sample values deviate from the "a" sample values by the same amount or more in 9 instances out of 28 where the analysis was made by chromic acid reduction, and in 5 instances out of 28 where furnace combustion was used. This analysis reveals that the initial and by far the greatest error, in a comparative study of this nature, is made at the time the samples are taken.

It was mentioned earlier in this paper that, as pointed out by Anderson and Byers (1), there has been no satisfactory method for detecting the presence in soils of small quantities of relatively inert (non-organic) carbon such as charcoal and cinders. The results of this study indicate that such inert forms of carbon may be estimated as the difference between total carbon by furnace combustion and organic carbon by chromic acid reduction, provided the amounts present are in excess of the experimental error inherent in the two methods.

The consistency of performance of the reduction method is shown by the fact that, on the average, duplicate determinations checked within 0.89 per cent, whereas in the case of furnace combustion the difference between duplicates averaged 1.20 per cent of the carbon present. This fact, combined with

its close agreement with the admittedly more accurate furnace combustion method, indicates that Schollenberger's chromic acid reduction method is satisfactory for the determination of organic carbon in soil.

TABLE 4

*A comparison of Schollenberger's chromic acid reduction method for organic soil carbon with furnace combustion*

Light-colored soils

RALEIGH FIELD			EWING FIELD		
Sample number	Carbon		Sample number	Carbon	
	Furnace combustion	Chromic acid reduction*		Furnace combustion	Chromic acid reduction*
	<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
9393a	1.34	1.35	9422a	1.16	1.17
9393b	1.34	1.36	9422b	1.14	1.13
9394a	1.29	1.29	9423a	1.23	1.25
9394b	1.27	1.27	9423b	1.22	1.23
9397a	1.41	1.43	9426a	1.05	1.06
9397b	1.40	1.41	9426b	1.07	1.08
9398a	1.47	1.47	9427a	1.03	1.02
9398b	1.44	1.46	9427b	1.03	1.05
9402a	1.22	1.26	9431a	1.07	1.06
9402b	1.22	1.23	9431b	1.09	1.08
9404a	1.04	1.05	9432a	1.03	1.05
9404b	1.02	1.03	9432b	1.03	1.02
9405a	1.15	1.16	9433a	1.05	1.06
9405b	1.17	1.15	9433b	1.09	1.09
9409a	1.15	1.14	9437a	0.79	0.80
9409b	1.13	1.14	9437b	0.78	0.81
9410a	0.93	0.92	9438a	1.00	1.01
9410b	0.91	0.89	9438b	1.01	1.02
9411a	1.00	0.99	9439a	1.06	1.06
9411b	1.00	0.99	9439b	1.06	1.07
9415a	1.16	1.17	9443a	1.21	1.19
9415b	1.13	1.13	9443b	1.21	1.21
9416a	1.00	1.00	9444a	0.91	0.92
9416b	1.02	1.02	9444b	0.92	0.92
9417a	1.03	1.02	9445a	1.04	1.06
9417b	1.02	1.00	9445b	1.04	1.04
9421a	1.17	1.16	9449a	1.25	1.26
9421b	1.18	1.16	9449b	1.24	1.23

\* Using new factor: 1 ml. 0.2 *N* titrant = 0.138 per cent organic carbon.

As a final check on the correctness of the empirical factor (1.15) for converting the theoretical value of milliliters of titrant used to percentage of carbon,



all of the 76 wet combustion values from tables 2, 3, and 4 were calculated as percentage of their corresponding dry combustion values. An average of 99.97 per cent was obtained which corresponds to essentially the same factor; namely, 1.1497.

Two samples per hour was found to be the maximum rate of analysis by furnace combustion, whereas at least three samples per hour can be determined with comparative ease by the chromic acid reduction procedure as outlined. Since the latter is a reduction method, it is unaffected by the presence of carbonates, a point which gives it considerable advantage over those methods that measure evolved carbon dioxide.

TABLE 5  
*Analysis of data in table 4*  
Comparison of analytical methods

SOURCE OF SAMPLE	NUMBER OF SAMPLES	NUMBER OF CASES IN WHICH DEVIATION OF CARBON VALUES BY REDUCTION METHOD FROM THOSE BY FURNACE COMBUSTION WAS—			STANDARD DEVIATION
		<2 per cent	2-3 per cent	>3 per cent	Per cent of combustion value
Raleigh field.....	28	26	1	1	1.24
Ewing field.....	28	27	0	1	1.18

Comparison of "a" and "b" samples

ANALYTICAL METHOD	NUMBER OF SAMPLES	NUMBER OF CASES IN WHICH CARBON IN "b" SAMPLE DIFFERS FROM THAT IN "a" SAMPLE BY—			STANDARD DEVIATION
		<2 per cent	2-3 per cent	>3 per cent	Per cent of "a" value
Chromic acid reduction.....	28	19	6	3	1.90
Furnace combustion.....	28	23	4	1	1.50

#### SUMMARY

A critical examination of Schollenberger's method for determining soil organic carbon by the reduction of chromic acid is reported. Modifications of this procedure by other investigators have been found less desirable than the original, since they have impaired one or more of its desirable features; namely, simplicity, rapidity, or accuracy.

Compared to furnace combustion, Schollenberger's method offers the following advantages: (a) it is approximately 50 per cent more rapid, (b) it is unaffected by the presence of carbonates in the sample, and (c) it does not determine inert carbon.

The conditions of time and temperature of oxidation by chromic acid reduction give uniformly incomplete oxidation of soil organic carbon. A conversion factor of 1.15 is required to bring carbon values by this method into agreement with furnace combustion data.

The analytical error of the reduction method, although slightly greater than that of the furnace combustion method, is shown to be less than the error in a commonly accepted method of sampling; hence the accuracy of this method is adequate for the purpose intended.

#### REFERENCES

- (1) ANDERSON, M. S., AND BYERS, H. G. 1934 The carbon-nitrogen ratio in relation to soil classification. *Soil Sci.* 38: 121.
- (2) BRUNSON, A. M., AND LOVE, H. H. 1924 Student's method for interpreting paired experiments. *Jour. Amer. Soc. Agron.* 16: 60.
- (3) DEGTJAREFF, W. TH. 1930 Determining soil organic matter by means of hydrogen peroxide and chromic acid. *Soil Sci.* 29: 239.
- (4) HECK, A. F. 1929 A method for the determination of total carbon and also for the estimation of carbon dioxide evolved from soils. *Soil Sci.* 28: 225.
- (5) SCHOLLENBERGER, C. J. 1927 A rapid approximate method for determining soil organic matter. *Soil Sci.* 24: 65.
- (6) SCHOLLENBERGER, C. J. 1931 The determination of soil organic matter. *Soil Sci.* 31: 483.
- (7) SMITH, G. F. Ortho-Phenanthroline. G. Frederick Smith Chemical Company, Columbus, Ohio.
- (8) TIURIN, I. V. 1931 A new modification of the volumetric method of determining soil organic matter by means of chromic acid (Russian with English summary). *Pedology* 5-6: 36.
- (9) WALKLEY, A., AND BLACK, I. A. 1934 An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Sci.* 37: 29.
- (10) WHITE, J. W., AND HOLBEN, F. J. 1925 Perfection of chromic acid method for determining organic carbon. *Jour. Indus. and Engin. Chem.* 17: 83.
- (11) WINTERS, ERIC, JR., AND SMITH, R. S. 1929 Determination of total carbon in soils. *Jour. Indus. and Engin. Chem.* (Anal. Ed.) 1: 202.

# THE CHEMICAL AND BIOLOGICAL NATURE OF CERTAIN FOREST SOILS<sup>1</sup>

W. L. POWERS AND W. B. BOLLEN

*Oregon Agricultural Experiment Station*

Received for publication December 20, 1934

Some of the great forests of the world are in the Pacific Northwest. Although the soils producing these forests have been little studied, it would seem that soil science may here render a service to forestry comparable to what it has rendered agriculture. Forest litter protects soil from erosion, increases absorption, and conserves water supply. It also is the parent material of underlying organic layers and, as such, largely determines the course of decompositions yielding humus and plant nutrients.

Although scientific investigation of forest soils has in the past been carried on mainly by the Forest Experiment Stations of northern Europe, several American investigators have recently made contributions to this field. It is now recognized that the different forest floors yielded by hardwood, coniferous, and mixed stands of timber with their accompanying ground covers, favor different types of decomposition and nitrogen transformation. Forest nutrition and development are thus directly influenced, and a study of the various factors concerned should be of value in forest maintenance, forest development, and the transformation of forest to agricultural land.

In a previous report by Powers (4) on the characteristics of nine north-western forest soil profiles, evidence was presented that the fermenting and humified layers are of chief importance in supplying nutrients to forest growths. Herein is reported a study of the chemical and microbiological characteristics of two Pennsylvania and two western Oregon forest soil profiles. The Oregon soils have been further employed during the past biennium in forest nursery and greenhouse fertilizer experiments in which the nitrogen economy in these forest soils has been given special attention.

## SOME CHEMICAL CHARACTERISTICS OF PENNSYLVANIA AND WESTERN OREGON FOREST SOILS

Profile samples of DeKalb and Upshaw soil series from Pennsylvania<sup>2</sup> and of Olympic and Aiken soil series from the Peavy Arboretum of Oregon State

<sup>1</sup> Published as technical paper 233 with the approval of the director, as a contribution from the Oregon Agricultural Experiment Station.

<sup>2</sup> The Pennsylvania forest soil profile samples were collected by Professor T. J. Starker, of School of Forestry, Oregon State College, while doing graduate work at Pennsylvania State College, and by Mr. Walter U. Garstka, instructor in the School of Forestry at Pennsylvania State College.



TABLE 1  
*Fertility in four forest soils*

	pH	ORG. M.*	TOT. N†	BASE EXCH. CAP. MGM. PER 100 GM.
<i>Pennsylvania forest soils</i>				
DeKalb		<i>per cent</i>	<i>per cent</i>	
Litter.....	4.00	94.3	0.6125	10.6
"F" layer.....	4.71	90.6	1.3020	10.6
"H" layer.....	4.48	78.0	1.5029	10.8
A ("HS") layer.....	4.48	3.22	0.0690	8.9
A <sub>2</sub> .....	4.12	1.05	0.0182	2.6
B <sub>1</sub> .....	3.96	1.68	0.0988	12.2
B <sub>2</sub> .....	4.56	1.51	0.0714	3.6
B <sub>3</sub> .....	4.63	0.50	0.0406	1.7
C.....	4.55	0.50	.....	3.6
Upshaw:				
Litter.....	....	95.8	0.8540	10.3
"F" layer.....	....	63.1	1.0052	27.1
"H" layer.....	5.07	7.68	0.3066	35.5
B <sub>1</sub> .....	5.68	6.46	0.2330	14.9
B <sub>2</sub> .....	5.68	1.77	0.0518	14.4
C.....	5.22	1.55	0.0389	13.5
<i>West Oregon forest soils</i>				
Aiken (Peavy Arboretum):				
Litter.....	5.56	79.74	0.9030	27.4
"F" layer.....	6.06	78.31	1.0710	33.7
"H" layer.....	4.55	67.05	1.1200	42.1
A <sub>1</sub> .....	5.39	35.44	0.6440	19.5
A <sub>2</sub> .....	5.62	5.18	0.1848	12.0
B.....	5.52	2.86	0.1120	17.1
C.....	5.39	1.53	0.0364	13.9
Olympic (Peavy Arboretum):				
Litter.....	6.49	84.68	0.8470	24.2
"F" layer.....	6.15	63.50	1.1340	40.8
"H" layer.....	6.61	59.56	0.7630	33.3
A <sub>1</sub> .....	6.38	13.28	0.3858	25.1
A.....	6.66	4.14	0.1596	18.4
B.....	6.00	1.91	0.0630	16.6
C.....	5.56	1.29	0.0196	18.5

\* Organic matter determinations were made by the modified J. B. Rather method (*Ark. Agr. Exp. Sta. Bul.* 140, 1907) as adapted by L. T. Alexander and H. G. Byers (*U. S. Dept. Agr. Tech. Bul.* 317, 1932).

† Determined by E. F. Torgerson.

College subjected to partial chemical analyses (table 1) show that the organic matter extends deeper in the western Oregon profiles and that nitrogen extends down with it. The maximum nitrogen content in the soil profiles is found

approximately at the boundary zone of the fermenting (F) and humified (H) layers. Base exchange capacity is also maximum at about this zone. Feeding roots are found massed at this zone or just below it. DeKalb soil is apparently more aged, most acid, and lowest in base exchange capacity. The profile characteristics of these four soils confirm the data previously reported for nine northwestern forest soils by Powers (4).

The "F" layer of Aiken and of Olympic silty clay loam under Douglas fir [*Pseudotsuga taxifolia* (La Marck) Britt] forest cover contained approximately 9 and 13 tons an acre of organic matter respectively, where the whole corresponding forest floor was approximately 10 and 16 tons. The nitrogen content slightly exceeded 1 per cent in the "F" layers. Fine feeding roots are massed just below this in the surface of the A<sub>1</sub> layer, apparently taking up nitrates promptly. At the end of a protracted dry season, the moisture content of the "F" and "H" layers in Aiken and Olympic soil profiles averaged 19 per cent.

#### MICROÖRGANISMS IN FOREST SOIL PROFILES

Preliminary investigations of profiles from pine, fir, redwood, juniper and spruce forests show the prevalence of certain characteristics in common, regardless of soil or forest type (table 2). Litter in all cases had the highest water capacity and harbored great numbers of microörganisms; when moist it yielded higher counts than underlying layers. "F" and "A" horizons generally contained the greatest numbers of all classes of microörganisms. H-layers were not well developed; traces of H-material could often be found, but in most cases could not be adequately sampled. All litter and "F" layers were markedly acid; they also often yielded water-soluble phosphate and nitrate when these were absent in lower layers.

Molds were much less variable in numbers than bacteria and actinomycetes; this was true not only of the various horizons of a given profile, but also of different profiles. The most numerous molds were penicillia; mucors and aspergilli, although much less abundant, were next in order and increased proportionally with depth. DeKalb horizons from Pennsylvania hardwood forest gave contrasting results, in that molds were especially abundant, exceeding bacteria in both "F" and "H" layers, and actinomycetes were found only in the litter.

Incubation of profile samples moistened to one-half water-holding capacity for 2 weeks at 28°C. approximately doubled mold counts in "F" and "A<sub>1</sub>" horizons, while in lower horizons the increase, though numerically small, was tenfold. Effects of incubation on bacteria and actinomycetes were irregular, but a reciprocal relation between these two groups was frequently exhibited. Moistening and incubating dry litter caused enormous increases in all microörganisms. Vigorous nitrification was found to proceed in the litter and "F" layers of a spruce profile. Nitrates were absent in the sample when collected. During storage in the natural moist condition, however, nitrates accumulated

until, after 17 months, the litter contained 2250 p.p.m. and the "F" layer 550 p.p.m. nitrogen as  $\text{NO}_3$ .

TABLE 2  
*Microorganisms in forest soil profile\**

SAMPLE	H <sub>2</sub> O (WATER-FREE BASIS)	NUMBERS PER GRAM, WATER-FREE BASIS		
		Bacteria	Actinomycetes	Molds
	<i>per cent</i>			
1. <i>DeKalb</i> silt loam air dry samples of 4/23/32 incubated at 28° and approximately 1/2 saturation for two weeks 6/14/33				
Litter.....	566	4,320,000	2,520,000	2,398,000
F-layer.....	344	4,883,000	None	7,394,000
H-layer.....	212	9,570,000	None	13,200,000
A*.....	23.5	1,413,000	None	1,000,000
2. <i>Aiken Silt Loam</i> —field condition, not incubated				
Litter.....	35.1	13,600	13,600	129,200
F.....	70.9	1,208,000	490,000	315,000
H.....	62.6	11,573,000	261,000	293,000
A, 0-6".....	33.7	667,000	95,000	65,300
A, 6-15".....	34.6	3,672,000	612,000	53,000
B, 15-36".....	33.9	2,448,000	1,360,000	19,000
C, 4-4½".....	39.5	392,000	10,000	1,600
3. <i>Olympic Silt Loam</i> —field condition, not incubated				
Litter.....	25.0	66,780,000	882,000	10,100
F.....	223	47,538,000	11,628,000	85,500
H.....	223	34,542,000	9,234,000	171,000
H, transition.....	147	7,627,000	4,734,000	65,800
A <sub>1</sub> .....	6.9	1,980,000	642,000	37,500
A <sub>2</sub> .....	31.9	4,323,000	732,000	12,000
B.....	38.9	596,000	78,000	1,400
C.....	63.4	175,000	80,000	3,000

\* No *Azotobacter* found in A.

#### EARTHWORMS AND OTHER MACROORGANISMS

A large species of earthworm and also moles and pocket gophers were observed to be active in cut-over and in forested land. Darwin (2) estimated that in England, 0.22 acre-inch passed through the body of earthworms a year and that the number of earthworms in some English soils was approximately 27,000 an acre. Bear (1) reported approximately 1,000,000 an acre in Ohio soil.

The number of earthworms based on several tests for western Oregon soils affected by tree cover was estimated. In Sites silty clay loam from which Douglas fir had been cut, the earthworms numbered approximately 250,000

an acre. In Willamette silty clay loam, under soft maple, they were estimated at 500,000 and in newly cultivated soil manured the year previous, earthworms were found present at the rate of approximately 1,500,000 an acre. Soil erosion plats on this soil type 0.001 acre in area, lost from 50 to 132 earthworms into the catch cans in a 3-months' period beginning February 12, 1935.

Earthworm castings were found in the fir forest under the litter in the crumb-mull on top of the mineral soil. The castings were collected from the surface on cut-over land where there was little litter. Chemical tests of earthworm castings and related materials are shown in table 3.

The work of earthworms appears to have little effect on reaction. There is evidence of a build-up in base exchange capacity, and the nitrogen and organic matter are much higher in the casting than in the parent soil.

TABLE 3  
*Chemical characteristics of earthworm castings and related materials\**

	MAPLE AND GRASS LITTER	SOIL	CASTINGS
<i>From Willamette silty clay loam—under soft maples, collected O. S. C. Campus, 3/4/35:</i>			
Reaction value, pH.....	6.74	6.50	6.80
Base exchange capacity, <i>m.e. per 100 gm.</i> .....	34.50	7.68	8.91
Organic matter, <i>per cent.</i> .....	67.50	3.17	9.02
Total nitrogen, <i>per cent.</i> .....	0.994	0.150	0.397
<i>From Sites silty clay loam—cut-over fir land. NE. Q. Sec. 10, Tp 13 S; R 6 W Wm Mer Ore.:</i>			
Reaction value, pH.....	6.7	6.20	6.20
Base exchange capacity, <i>m.e. per 100 gm.</i> .....	14.30	11.40	27.13
Organic matter, <i>per cent.</i> .....	73.14	6.52	34.66
Total nitrogen, <i>per cent.</i> .....	.....	0.228	0.672

\* Mr. Clarence Burnham, research fellow in soils, assisted in these determinations.

Earthworms and related macroorganisms serve as colloid mills to generate an intimate mixture of fine organic and inorganic matter. To test the value of their activity, duplicate series of jars of loam were arranged with water jackets to confine earthworms. Two jars were used as checks; a second pair received earthworms; a third pair, worms and green clover clippings; and a fourth, clippings only.

Barley grown in these jars yielded definitely more where the worms were at work. Other culture jars of sandy loam to which earthworm castings were added to the amount of 5 per cent dry weight show growth response indicating that the beneficial effect is partly chemical.

#### NITROGEN AVAILABILITY IN FOREST SOIL LAYERS

A study was made of the nitrate-supplying power of two forest soil profiles by adding sufficient material from each horizon to supply 1.5 gm. nitrogen to

TABLE 4  
Nitrogen availability in forest soil layers  
Determinations started January 27, 1932

FOREST SOIL	TREATMENT OF 3,800 GM. SAND	NITRO- GEN IN LITTER	MATERIAL REQUIRED FOR 1.5 GM. N	OAT HAY PRODUCED		N TOTAL	NITRO- GEN RE- MOVED IN CROP
				Fresh	Dry		
		<i>per cent</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>
Astoria fir land.....	Litter	0.989	152.00	34.94	10.48	0.609	0.0638
	F layer	1.199	125.10	43.20	12.96	0.652	0.0845
	H layer	0.655	229.00	43.25	12.97	0.536	0.0695
	H-S	0.293	511.00	66.75	20.02	0.553	0.1107
	Soil	0.155	967.00	3.95	1.18	0.815	0.0096
	Solution, N	.....	.....	2.57	0.77	0.848	0.0065
	NaNO <sub>3</sub>	16.000	9.37	.....	.....	.....	.....
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	20.000	7.50	.....	.....	.....	.....
	R. Blood	12.000	12.50	.....	.....	.....	.....
	Complete solution	.....	.....	100.13	30.04	0.695	0.2088
Pioneer camp, Ponder- osa pine land.....	Litter	1.060	141.50	23.90	7.17	0.599	0.0429
	F	1.177	127.00	18.50	5.55	0.506	0.0281
	H	0.861	174.00	43.68	13.10	0.498	0.0652
	H-S	0.179	836.00	10.31	3.09	0.465	0.0609
	Soil	0.092	1633.00	43.40	13.02	0.389	0.0506
	Solution, N	.....	.....	4.20	1.26	0.822	0.0104
	NaNO <sub>3</sub>	16.000	9.37	.....	.....	.....	.....
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	20.000	7.50	.....	.....	.....	.....
	R. Blood	.....	12.50	.....	.....	.....	.....
	Complete solution	.....	.....	94.27	28.28	0.579	0.1637

TABLE 5  
Nitrate in leachate from fallowed percolation tubes  
(Soil layers—1,900 gm. sand + 0.75 gm. N in forest-floor layers)

	FEBRUARY 10	FEBRUARY 22	MARCH 7	MARCH 20	TOTAL NITROGEN LEACHED, 6-WEEK PERIOD
	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
Astoria + 1,900 gm. sand:					
Litter 76 gm.....	2.4	3.5	1.5	2.0	9.4
F 62.5.....	2.8	2.0	0.4	Trace	5.2
H 114.5.....	2.5	0.7	0.2	Trace	3.4
HS 225.0.....	0.5	0.1	0.3	Trace	1.0
Sand X-1,900.....	Trace	0.0	0.0	0.0	Trace
L 76 + 40. CaCO <sub>3</sub> .....	3.0	3.0	0.5	2.5	9.0
Pioneer camp + 1,900 gm. sand:					
L 70.7.....	2.0	3.7	0.6	1.00	7.3
F 63.7.....	1.3	0.1	0.4	1.00	2.8
H 87.0.....	1.0	0.2	0.4	2.00	3.6
H-S 41.0.....	0.5	2.5	0.4	1.12	4.6
Sand X 1,900.....	Trace	Trace	0.0	0.00	Trace
L 70.7 gm. + 40 gm. CaCO <sub>3</sub> .....	7.5	2.0	0.5	0.63	9.6



culture jars containing 3,800 gm. of clean quartz sand. A culture solution lacking nitrogen was used to help keep the sand moist while oats were grown. The yield and nitrogen content were determined as shown in table 5. The maximum crop yield and nitrogen content were obtained where nitrogen was supplied in material from the H or H-S layer (see plate 1).

Parallel series of large glass percolation tubes were similarly prepared except that they were fallowed and leached each 2 weeks, and the nitrate in leachate was determined as reported in table 5. Copper sulfate proved most suitable for clarifying solutions for colorimetric determinations, which, however, are only approximate. Liming increased yield of nitrate slightly. Relative amounts of nitrate correspond to yields and nitrates removed in the cropped series. The writers plan a further study of the nitrogen economy of forest soils.

#### DISCUSSION

Data herein presented support those previously reported by Lunt (3) and show that the maximum absorptiveness for moisture or colloidalilty, maximum adsorptiveness or base exchange capacity, and maximum number of microorganisms and macroorganisms were found in the fermenting layers which contain approximately 75 per cent organic matter. Artificial mixtures of organic and inorganic soil colloids, varied by 20 per cent intervals, show a corresponding base adsorption curve.

The forest soil profiles from Pennsylvania, being more acid and lower in base exchange capacity, show more degeneration than do those from the Pacific Northwest.

The earthworms and related macroorganisms serve as colloid mills to generate this intimate mixture of fine organic and inorganic matter.

Feeding roots are massed in forest soils in or just below this organic layer. Lunt (3) has reported that 40 to 45 per cent of the exchangeable calcium in the whole profile is found in the humus portion, or the A1 horizon. Active organic matter may increase the soluble iron and perhaps phosphorus in the soil solution.

#### SUMMARY

Studies of forest soil profiles made at the Oregon Experiment Station show that the nutrient supplying power is centered in the F and H layers, especially as to bases and nitrates. Microorganisms and also macroorganisms are important in humus-nitrogen generation.

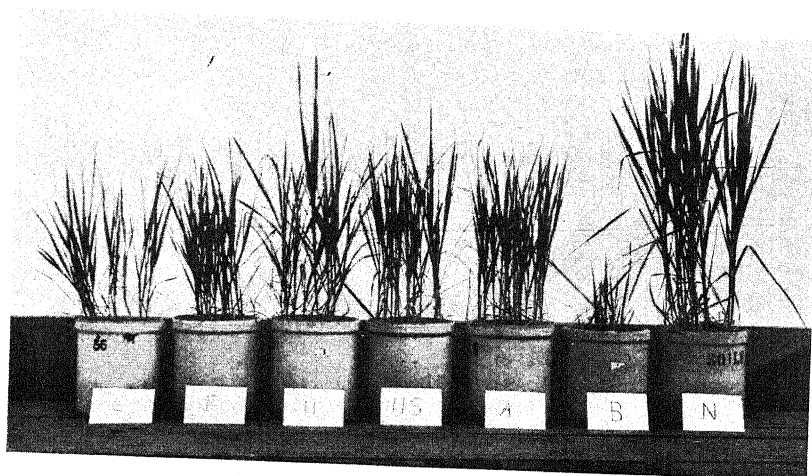
#### REFERENCES

- (1) BEAR, F. E. 1929 Fertilizers, p. 146. J. Wiley & Sons, N. Y.
- (2) DARWIN, CHARLES A. 1881 Generation of Vegetable Mold by Earthworms, chapter 3. D. Appleton & Co., New York.
- (3) LUNT, H. A. 1932 Discussion of significance of replaceable bases in organic soil horizons. *Amer. Soil Survey Assoc. Bul.* 13: 24.
- (4) POWERS, W. L. 1932 Characteristics of forest soils in northwestern United States. *Soil Sci.* 36: 1.

## PLATE 1

GROWTH OF OATS IN SAND CULTURES KEPT MOIST WITH CULTURE SOLUTION LACKING,  
NITROGEN, AND SUPPLIED WITH 1.5 GM. NITROGEN IN FOREST SOIL LAYERS

"Complete" nutrient solution at right





# MICROBIAL ACTIVITIES IN SOIL: II. ACTIVITY OF SPECIFIC GROUPS OF MICROBES IN RELATION TO ORGANIC MATTER TRANSFORMATION IN PALOUSE SILT LOAM<sup>1</sup>

S. C. VANDECAVEYE AND MELVIN C. ALLEN<sup>2</sup>

*Washington Agricultural Experiment Station*

Received for publication November 20, 1934

Although climatic environment and inherent soil characteristics are primary factors in controlling the biological activity in soil, the nature and quantity of potential food supplied by organic residues readily modify this activity. The profuse evolution of carbon dioxide and the sudden increase in number and activity of many different kinds of organisms following additions of organic residues to the soil have been the subject of extensive investigations, but the rôle of specific groups of microbes in relation to the activity of other groups and to the progressive steps in the process of organic matter transformation in the soil is not well known.

In the decomposition of straw by a mixed soil flora Norman (5) recognized the fact that there is a sequence in types of organisms. Waksman and Starkey (11) are of the opinion that frequently there is a sequence of organisms depending upon the nature of the organic residues as a source of energy. Results given in a previous publication (8) suggest that in the transformation of carbonaceous residues added to the soil there is a definite sequence of activity of important groups of microbes which appears to affect the development of other groups. The following data are presented in an attempt to elucidate further the activity of specific groups of microbes and their functions in the progressive steps in the transformation of organic residues in the soil.

## EXPERIMENTAL PROCEDURE

Unpublished data from three of a series of continuous wheat plots  $\frac{1}{8}$  acre in size and receiving the indicated field treatments for nine consecutive years show the following results<sup>3</sup>:

<sup>1</sup> Published as Scientific Paper No. 258, College of Agriculture and Agricultural Experiment Station, State College of Washington.

<sup>2</sup> Professor of soils and research assistant, respectively.

<sup>3</sup> The authors are indebted to the late H. F. Holtz for the data on these plots.

FIELD PLOT	ANNUAL TREATMENT PER ACRE	AVERAGE YIELD OF WHEAT PER ACRE	GAIN IN N PER ACRE,* EXCLUDING N ADDED BY FERTILIZER AND N REMOVED BY CROP
	<i>pounds</i>	<i>bushels</i>	<i>pounds</i>
104	Stubble returned	23.4	124.6
105	Straw 2700	34.5	1.3
	NaNO <sub>3</sub> 370		
107	Straw 2700	31.6	376.9
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 286		

\* Based on 3,500,000 pounds of dry soil.

The different behavior of the nitrogen and consequently of the organic matter in the soils of the two plots receiving the same amount of straw and also the same amount of nitrogen which, however, was supplied in different forms of fertilizer, prompted this investigation.

*Preparation of Soil Samples.*—In July, 1930, when the soil moisture content in the root zone approached the wilting point, representative samples of soil were obtained from each plot. Borings 1 foot deep were made with a soil auger at 48 points uniformly distributed on each plot, and sufficient soil was thus obtained to make the samples equivalent to 8 kgm. of dry soil. These were passed through a 6-mesh sieve several times to insure thorough mixing and to remove coarse organic residue. The soils were placed in jars, to which sufficient water was added to adjust the moisture to the normal field capacity of 20 per cent. The jars were covered and allowed to stand in the laboratory for 4 days to insure uniform moisture distribution and to give the microflora a chance to resume its normal functions. The soils were then removed from the jars and divided into two equal portions. One per cent finely ground wheat straw reenforced with enough ammonium nitrate to make the nitrogen content of the straw equivalent to 2.5 per cent was thoroughly mixed with one of each of the duplicate portions. Since a preliminary examination indicated that the number of Azotobacter in the field soil was small, each sample was inoculated with a heavy suspension of these organisms. A quantity equivalent to 1 kgm. of dry soil was removed from each sample for chemical and microbial analyses, and the remainder was placed into wide-mouth bottles and packed by gently jarring the bottles on the table. The bottles were connected with an absorption train for carbon dioxide determinations. The arrangement of the samples and soil treatments was as follows:

FIELD PLOT	FIELD TREATMENT PER ACRE	SOIL SAMPLE	LABORATORY TREATMENT PER KILOGRAM DRY SOIL
	<i>pounds</i>		<i>gram</i>
104	Stubble returned	1	Control
		2	Straw, 10
			NH <sub>4</sub> NO <sub>3</sub> , 0.68
105	Wheat straw, 2700	3	Control
	NaNO <sub>3</sub> , 370	4	Straw, 10
			NH <sub>4</sub> NO <sub>3</sub> , 0.68
107	Wheat straw, 2700	5	Control
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , 286		Straw, 10

*Determination of Microbial Activity.*—The experiment was carried on at room temperature, which ranged from 20 to 25°C. The production of carbon dioxide and the numbers of total bacteria, fungi, actinomyces, cellulose decomposing bacteria, and Azotobacter were determined at the beginning; after the first, second, fourth, seventh, eleventh, and sixteenth day of the experiment; and every week thereafter until the end of the fifteenth week, when the microbial activity remained relatively uniform and the interval between determinations was extended to 2 weeks.

The numbers of total bacteria were ascertained by the direct microscopic method, and those of the fungi, cellulose decomposing bacteria, and Azotobacter, by plating on selective media following essentially the same procedure as described in a previous publication (8). The numbers of actinomyces were determined by plating suitable dilutions of soil suspensions on albuminate agar media prepared according to Fred and Waksman (2) and adjusted to pH 8.0.

The samples for the determination of microbial development were prepared in the following manner: At each sampling the soil from each bottle was removed and passed three times through a 6-mesh sieve onto a clean paper. This procedure was considered helpful in producing a thoroughly mixed, representative sample and in promoting thorough aeration, which should prevent the occurrence of any possible anaerobic condition that otherwise might develop in the bottles during the course of the experiment. The small amounts of soil required for plating were weighed immediately, and those needed for the silica gel plates were air dried by spreading them thinly on clean papers. The remainder of the soil was returned to the bottles and packed by gently tapping the bottles on the table. The soil moisture content was maintained within narrow limits by addition of water when necessary.

*Chemical Analysis.*—Chemical analyses were made at intervals for soil reaction; organic carbon; total nitrogen; nitrate nitrogen; fats, waxes, and resins; hot-water-soluble substances; hemicelluloses; cellulose; protein; and lignin. These substances were determined: A, at the beginning of the experiment; B, 37 days later when the fungi had reached the peak of activity; C, at 100 days when the maximum activity of the Azotobacter had been reached; and finally D, at the end of the experiment. The samples for these analyses consisted of quantities equivalent to 1000 gm. of dry soil for the first period and 800 gm. of dry soil for the other periods. These samples were air dried and stored until it was convenient to analyze them consecutively.

The total and nitrate nitrogen contents were determined by the Kjeldahl and phenoldisulfonic acid procedures respectively according to the official and tentative methods of analysis (1); the organic carbon contents, by the wet combustion method of Friedemann and Kendall (3); and the pH values, by means of the quinhydrone electrode in suspensions of one part of soil to five parts of water. The fractionation of the organic matter was conducted according to the method outlined by Waksman and Stevens (10).

## EXPERIMENTAL RESULTS

The trend of  $\text{CO}_2$  production and of the activity of various groups of microbes is illustrated in figures 1, 2, and 3. As can be noted, the addition of 1 per cent wheat straw to soils which were assumed to be normal in microbial activity at the time this organic residue was applied caused an immediate profuse production of  $\text{CO}_2$  and a somewhat delayed but nevertheless great increase in numbers of bacteria, fungi, and actinomyces. Whereas the production of  $\text{CO}_2$  was greatest the first day, the increase in numbers of microbes lagged considerably and did not reach a maximum until about one month later when the production of  $\text{CO}_2$  was relatively low. A similar occurrence has been observed previously (8).

It may be assumed that as the microbial cells multiplied, more of the liberated  $\text{CO}_2$  was used up by the rapidly increasing population. This might account for a brief lag period between  $\text{CO}_2$  production and multiplication of organisms, as a part of the new food supply was probably used up before active multiplication of microbial cells took place. It does not explain the protracted lag which extended over a period of several weeks.  $\text{CO}_2$  production and numbers of organisms did not occur in comparable proportions as long as considerable quantities of readily available organic compounds were present. Not until the decomposition of the straw had proceeded far enough to approach the conditions existing in soils 2, 4, and 6 was a relatively stable equilibrium reached in the activity of the important groups of microbes primarily concerned with the transformation of organic matter. Evidently the rate of  $\text{CO}_2$  evolution cannot always be considered as a true index of the numbers of organisms at work.

The bacteria as a group were the quickest to take advantage of the readily available food supply, but they were followed very closely by the actinomyces in two of the three soils. Since the number of fungi did not rise materially during the first four or five days, it would seem that they were unable to compete successfully with the other groups at that time. The fungi may have been very active, however, with resulting increase in size of colonies and extent of mycelium, which is very difficult to detect by plant count.

The activity of cellulose decomposing bacteria and *Azotobacter* was not appreciably affected by the additions of straw and soluble nitrogen until the numbers of bacteria, actinomyces, and fungi were distinctly on the decline; that is, about 50 to 60 days after the experiment was started. Hence, the cellulose decomposing bacteria, in as far as numbers are concerned, were relatively inactive while the supply of cellulose was greatest and reached their peak of activity only after the competition of the more vigorous groups had abated and a large part of the cellulose had been decomposed. Even then their numbers failed to reach important proportions.

Parallel with the development of cellulose decomposing bacteria was that of *Azotobacter* which, like the former, failed to reach large numbers. Both



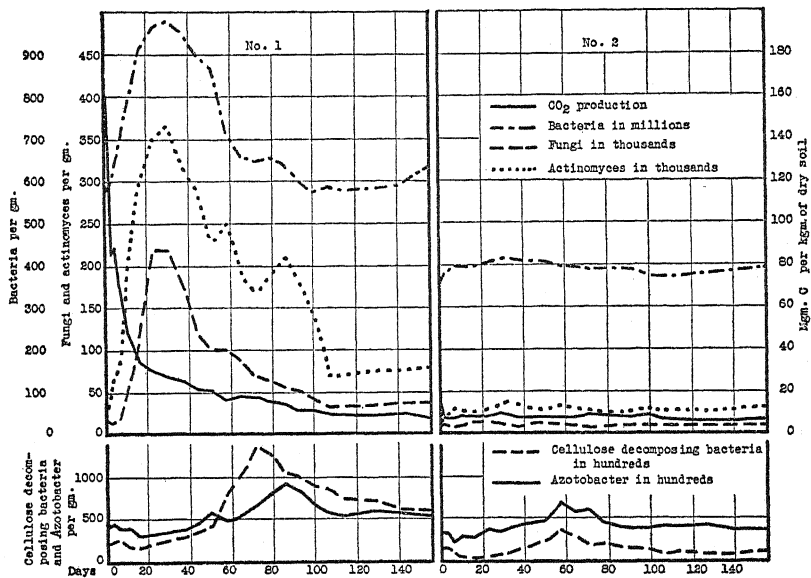


FIG. 1. CO<sub>2</sub> PRODUCTION AND MICROBIAL DEVELOPMENT IN SOIL TO WHICH STUBBLE ONLY WAS RETURNED FOR 9 CONSECUTIVE YEARS

No. 1, soil treated with 1 per cent straw supplemented with  $\text{NH}_4\text{NO}_3$ ; No. 2, control

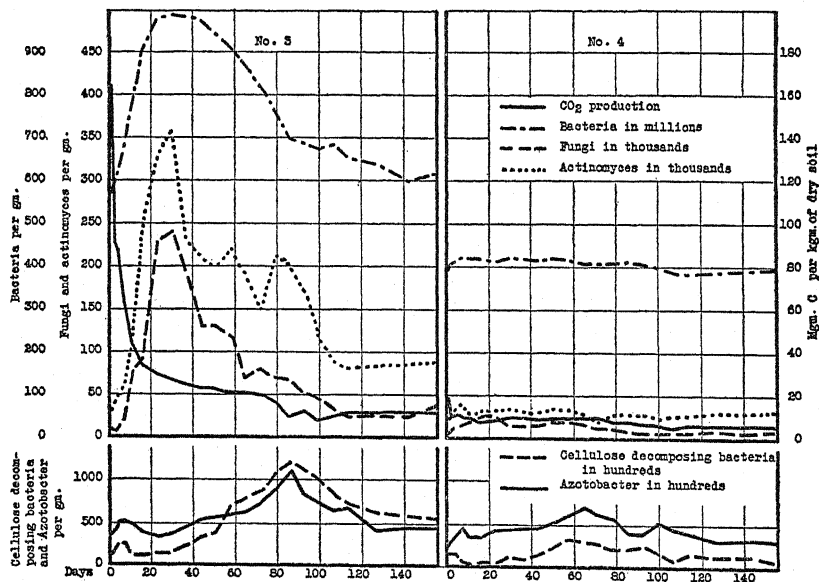


FIG. 2. CO<sub>2</sub> PRODUCTION AND MICROBIAL DEVELOPMENT IN SOIL RECEIVING 2,700 POUND OF STRAW AND 370 POUNDS NITRATE OF SODA ANNUALLY FOR 9 YEARS

No. 3, soil treated with 1 per cent straw supplemented with  $\text{NH}_4\text{NO}_3$ ; No. 4, control

of these groups appeared to be better able to utilize the more resistant parts of the straw than the three other groups.

One of the objects of adding large quantities of straw to soils 1, 3, and 5 was to study the effect of this carbonaceous residue on the development of Azotobacter and incidentally on non-symbiotic nitrogen fixation. A previous study (8) has revealed that the activity of Azotobacter both in terms of numbers and in terms of nitrogen fixation may be stimulated conspicuously when the soil has received large quantities of cellulose and other organic residues. The results were obtained on soils taken from the field at a time when Azotobacter was very active. Data in another publication (7) indicate that there

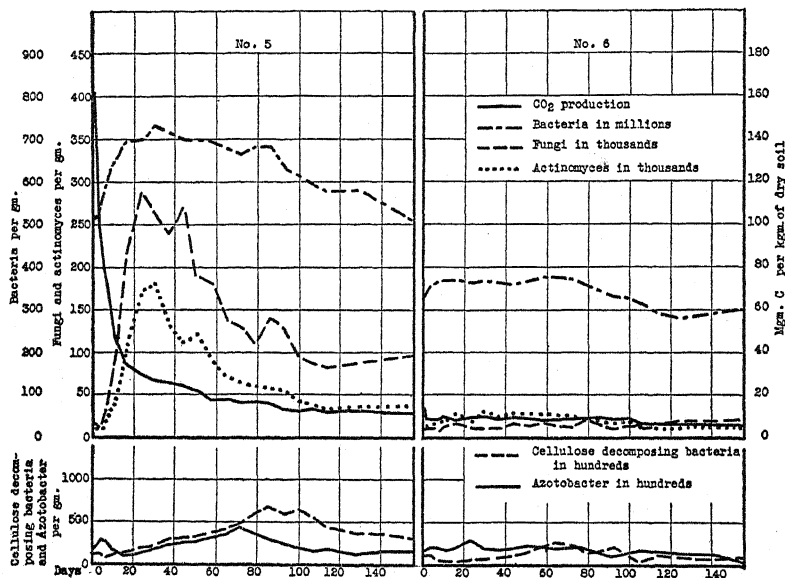


FIG. 3. CO<sub>2</sub> PRODUCTION AND MICROBIAL DEVELOPMENT IN SOIL RECEIVING 2,700 POUNDS OF STRAW AND 285 POUNDS SULFATE OF AMMONIA ANNUALLY FOR 9 YEARS

No. 5, soil treated with 1 per cent straw supplemented with  $\text{NH}_4\text{NO}_3$ ; No. 6, control

was considerable fluctuation in numbers of Azotobacter in field plots lying adjacent and receiving similar treatments to the ones used for the work here presented. As has been stated already the number of Azotobacter in the latter soils was small and inoculation with an active suspension of these organisms was necessary. In spite of this inoculation and contrary to previous results (8) the number of Azotobacter never reached sufficient proportions to fix significant amounts of atmospheric nitrogen. The data in table 1 actually show a loss of nitrogen in two of the three samples that had been treated with 1 per cent of straw. The control samples, on the contrary, gained in total nitrogen, but this gain cannot be attributed to the activity of Azotobacter.

The curves in figures 1, 2, and 3 (samples 2, 4, and 6) indicate that the

repeated field applications of wheat straw and nitrogen fertilizers did not significantly affect  $\text{CO}_2$  evolution or the activity of various groups of microbes. This is confirmed largely by the data in table 1, showing that no important quantities of organic matter have accumulated as a result of these treatments. The small increases occurring can be accounted for by the partially decomposed residue which no doubt accumulated under the existing climatic conditions.

Although the total  $\text{CO}_2$  production, as shown in table 1, was greatest in sample 5 (the soil which had received ammonium sulfate and straw in the field), the microbial activity proved to be less than in either sample 1 (the soil receiving only stubble in the field) or sample 3 (the soil treated with straw and sodium nitrate in the field), in so far as could be ascertained by total numbers in the groups of organisms studied. Furthermore, the microbial activity in sample 5 was of a different nature. The numbers of bacteria and actinomycetes were consistently lower and the numbers of fungi considerably higher than in

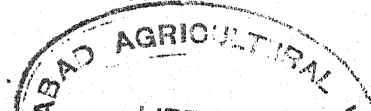
TABLE 1  
*Carbon dioxide production and organic carbon and nitrogen balance*

SOIL	C		LOSS	N		LOSS OR GAIN	C PER KG. OF DRY SOIL
	Beginning	End		Beginning	End		
	<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>		
1	2.25	2.01	8400	0.153	0.148	-175	2.24
2	1.70	1.56	4900	0.153	0.156	+105	1.29
3	2.33	2.08	8750	0.156	0.156	00	3.41
4	1.77	1.58	6650	0.156	0.165	+315	1.58
5	2.32	2.10	7700	0.161	0.156	-140	3.44
6	1.85	1.67	6300	0.161	0.180	+665	1.34

\* Based on 3,500,000 pounds of dry soil.

the other two samples. The same tendency prevailed in sample 6 (soil from the same plot) but to a much smaller degree, because it had not received the 1 per cent straw in the laboratory. Under certain soil conditions the favorable growth of fungi, such as occurred in sample 6, might be expected to result from increased acidity which is often brought about when ammonium sulfate is applied repeatedly. Such an explanation does not hold in this case, as the pH values of samples 5 and 6, as indicated in table 2, were greater than those of the soil to which stubble alone had been added. Since the only apparent chemical difference in this soil as compared with the others is a possible accumulation of sulfate compounds, it seems reasonable to assume that the residual effect of sulfate may account for the observed difference in biological activity. Thus it appears that specific soil characteristics either inherent or brought about by soil management may have a determining effect upon the particular nature of the prevailing microbial activity even though the original food supply is the same.

Regardless of the variation in nature of microbial activity, it is evident that



during the first stages of organic matter transformation following the addition of 1 per cent straw the production of  $\text{CO}_2$  was not a true index of microbial propagation. These first stages of decomposition were marked by a distinct sequence of organisms with the bacteria as a group taking the lead, followed closely by the actinomyces and the fungi respectively in two of the three soils, and by the actinomyces and fungi simultaneously in the other soil. The cellulose decomposing bacteria and *Azotobacter* did not increase in numbers materially until the activity of the three other groups had subsided.

#### FUNCTIONS OF SPECIFIC GROUPS OF MICROBES IN ORGANIC MATTER TRANSFORMATION

Tenney and Waksman (6) have shown that aerobic decomposition of plant residues takes place in definite steps depending upon the chemical composition of the materials. Unlike the majority of plant residues in which the hemicelluloses and celluloses usually make up the largest fraction, soil organic mat-

TABLE 2  
*Soil reaction and nitrate nitrogen accumulation*

SOIL	pH VALUES		NO <sub>3</sub> IN P.P.M. OF N			
	Beginning	End	A 0 days	B 37 days	C 100 days	D 156 days
1	6.5	6.4	39	13	46	67
2	6.5	6.5	13	12	29	33
3	7.2	7.0	57	30	65	46
4	7.2	7.0	13	24	38	37
5	6.6	6.5	53	50	90	97
6	6.6	6.5	13	26	49	66

ter is low in these constituents and the lignins and proteins constitute the largest part. When undecomposed plant residue is added to the soil in field practice, it usually amounts to a relatively small percentage of the soil organic matter and is always a small proportion of the entire soil mass. Therefore, methods in organic matter fractionation that can be depended upon to give satisfactory results in showing the steps in the transformations of plant residue decomposing by itself without being mixed with soil can at best give only approximate results when used to determine the course of transformation of plant residue added to the soil in amounts consistent with field practice. Nevertheless, as is shown by the data in table 3, periodical determinations of various organic complexes during the process of organic matter transformation in soil indicate certain definite trends.

An examination of these data reveals marked changes in some constituents of the organic matter. At the beginning of the experiment the percentage of hot-water-soluble substances in the organic matter of the soils receiving 1 per cent straw was about twice as large, and that of the hemicelluloses and

celluloses more than twice as large as the percentage of these materials in the control soils. This comparison shows how the soil organic matter constituents may be affected when plant residues are returned to the soil and gives an idea of the magnitude of work that is to be performed by the microbes whose function it is to restore the equilibrium of these constituents to its original status.

The other extracts which contain the fats, waxes, and resins constitute only a small fraction of the organic matter, and it can be noted that the percentage of these constituents was not materially affected by soil treatments or by microbial activity.

During the first 37 days of incubation the carbohydrate compounds, including sugars, starches, hemicelluloses, and celluloses, contributed by the straw disappeared rapidly, whereas there was a slight increase in percentage of lignins and proteins. In the course of the following two months when the activity of bacteria, actinomycetes, and fungi was on the decline and the cellulose decomposing bacteria and *Azotobacter* were in their most active stage the hot-water-soluble substances began to accumulate in two of the three soils. The hemicelluloses and celluloses continued to disappear rapidly, whereas the relative amounts of lignins and proteins continued to rise. The last period covering about two months was marked by a relatively small decline in numbers or organisms in each of the five groups. The relative proportion of water-soluble materials in the organic matter continued to increase, whereas the hemicelluloses and celluloses continued to disappear. The percentages of lignins and proteins also continued to increase, the former on account of its resistance to decomposition and the latter as a result of protein synthesis by microorganisms.

The behavior of various organic complexes during the course of the organic matter transformation is well illustrated in figure 4, which is representative of the different soils employed. The trend in cellulose decomposition, which was similar in both the treated and control soils, is worthy of attention. In spite of the fact that the control soils maintained a very uniform microbial activity the percentage of cellulose in the organic matter dropped in a similar manner to that in the treated soils, which had a fluctuating microbial activity and were supplied with an abundance of cellulose in the form of straw. It should be noted in this connection that the soils employed for this work were obtained from plots supporting wheat that was approaching maturity. Hence, the control samples contained considerable amounts of fresh root tissue supplying readily available cellulose, and this may account for the behavior of cellulose in these samples. The gradual accumulation of hemicelluloses in the control soils is, as indicated in figure 4, in direct contrast with the behavior of these substances in the other soils and cannot be explained on the same basis as the behavior of the celluloses.

The steady increase in amounts of water-soluble material following the first 37 days' period of decomposition is of interest in that it occurred in the

control soils having a uniform microbial activity as well as in the treated soils under a fluctuating microbial activity and at a time when the numbers of bacteria, actinomycetes, and fungi were dropping rapidly. Although the actual quantities of these substances are small in comparison with the total organic matter content, it seems that the bacteria, actinomycetes, and fungi, which were quick in taking advantage of these compounds in the first stage of decomposition, would have prevented this accumulation if food relationships as stated by Waksman and Starkey (11) are the principal factors in the predominance of specific groups of microbes. There was no lack of available nitrogen to retard the growth of any of these groups, as can be seen from the

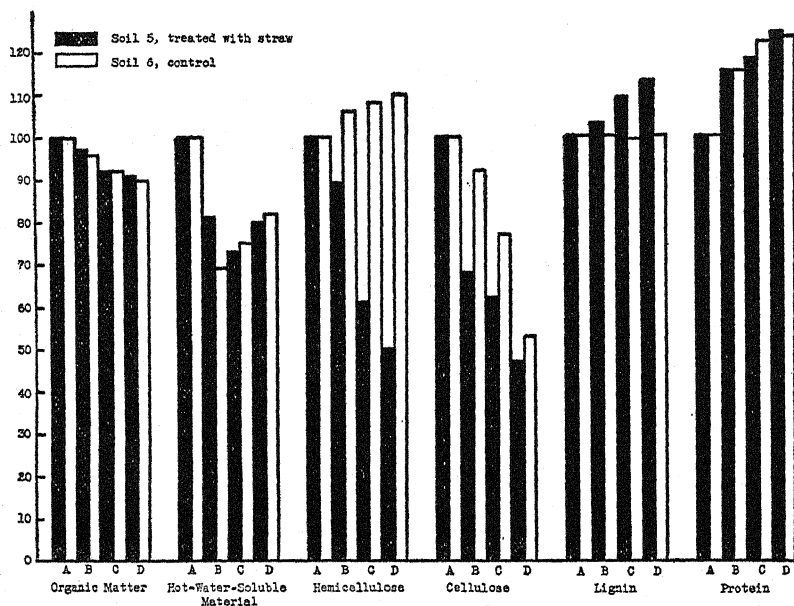


FIG. 4. TREND IN DECOMPOSITION OF ORGANIC COMPLEXES IN SOIL

A, beginning; B, 37 days; C, 100 days; D, 156 days

data in table 2. In all probability a large part of these accumulated products was of a secondary nature derived from microbial tissue and constituted less desirable food than the water-soluble substances in the plant residue. For similar conditions Norman (5) suggests that there is a production of toxic substances by specific groups of microbes which may result in a natural suppression of other groups.

From a comparison of the course of the various organic substances in the organic matter transformation as shown in table 3 and illustrated in figure 4 with the activity of specific groups of microbes in terms of numbers as indicated in figures 1, 2, and 3, it appears that the hot-water-soluble substances contributed by the straw were decomposed largely during the first 37 days and that

the bacteria as a group, because of their superior numbers and more rapid increase, were responsible for a large part of this decomposition.

The hemicelluloses and celluloses contributed by the straw appeared to be decomposed at a uniform rate during a period extending over approximately 80 days.

Heck (4) and Waksman and Skinner (9) attribute the principal rôle in the decomposition of cellulose materials to fungi. Judging from the numbers of

TABLE 3

*Proximate composition of soil organic matter at various periods: A, beginning; B, 37 days; C, 100 days; D, 156 days of incubation*

SOIL	ORGANIC MATTER	ORGANIC MATTER CONSTITUENTS*						TOTAL ACCOUNTED FOR
		Ether extract	Hot water extract	Hemi- cellulose	Cellulose	Protein	Lignin	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A1	3.88	1.88	7.06	6.56	9.66	28.66	40.30	94.12
2	2.93	1.23	4.44	2.94	4.11	31.62	48.63	92.97
3	4.01	2.01	7.07	6.34	10.62	29.33	40.82	96.19
4	3.06	1.57	4.05	2.68	4.11	30.73	47.44	90.58
5	4.00	2.44	8.09	7.18	8.65	28.12	41.68	96.16
6	3.19	1.66	5.64	3.10	3.24	31.73	49.15	94.52
B1	3.72	1.93	4.94	5.34	6.29	30.69	41.79	90.98
2	2.90	1.17	3.04	3.14	3.31	32.66	47.12	90.44
3	3.82	2.01	5.03	4.68	6.28	29.48	42.77	90.25
4	2.93	1.64	4.03	2.96	3.54	36.59	46.89	94.98
5	3.89	2.34	6.53	6.38	5.84	32.42	42.97	96.48
6	3.07	1.59	3.90	3.28	3.00	36.38	49.09	97.24
C1	3.52	2.10	5.79	3.56	5.19	33.08	44.16	93.88
2	2.76	1.30	3.47	3.28	2.62	35.79	47.19	93.65
3	3.67	1.93	5.88	3.30	5.83	33.90	44.18	95.02
4	2.82	1.87	5.67	3.02	2.56	37.97	46.28	97.37
5	3.70	1.94	5.89	4.40	5.36	33.13	45.34	96.06
6	2.94	1.46	4.22	3.34	2.51	38.62	48.82	98.97
D1	3.47	1.93	6.11	3.00	3.90	34.67	46.32	95.93
2	2.70	1.52	4.54	3.36	2.11	37.84	46.86	96.23
3	3.58	1.70	6.09	2.76	3.66	35.09	46.92	96.22
4	2.73	1.34	5.96	3.12	2.08	39.40	47.17	99.07
5	3.63	1.67	6.50	3.56	4.03	34.74	47.21	97.71
6	2.88	1.23	4.70	3.41	1.73	38.90	48.96	98.93

\* Percentages on basis of dry organic matter.

organisms in various groups, it appears that the bacteria and actinomyces as well as the fungi took an important part in the decomposition of these products.

The activity of the cellulose decomposing bacteria and *Azotobacter* never became very prominent, but their numbers increased considerably after a large part of the readily available substances contributed by the straw had been decomposed, suggesting that these organisms are better able to utilize the more resistant compounds of organic residues than are the other groups.

The fact that the relative proportion of lignins to organic matter in the control soils remained uniform throughout the experiment, whereas it increased steadily in the treated soils is an indication that the lignin compounds supplied by the straw remained largely untouched during the course of the experiment.

#### SUMMARY

The activity of specific groups of microbes and their functions in organic matter transformation were studied in Palouse silt loam obtained from three of a series of field plots following nine years of continuous cropping with wheat. Stubble was the only residue returned to one of the plots, whereas the others received annual treatments of straw with sodium nitrate and of straw with ammonium sulfate respectively. One per cent of finely ground wheat straw reinforced with sufficient ammonium nitrate to make the nitrogen content of the straw equivalent to 2.5 per cent was mixed with one of the duplicate samples used from each plot.

Frequent determinations of the numbers of specific groups of organisms, including total bacteria, actinomycetes, fungi, cellulose decomposing bacteria, and Azotobacter, and periodical analyses of various organic complexes were made in the laboratory.

During the first stages of decomposition of the organic residue in the soils the rate of  $\text{CO}_2$  evolution was not a true measure of the numbers of active microbes, as the former was most profuse during the first days, whereas the latter did not reach their maximum numbers until about five weeks later.

A sequence of activity of specific groups of microbes occurred during this period. The bacteria as a group took the lead but were followed closely by the actinomycetes and fungi.

The activity of the cellulose decomposing bacteria and Azotobacter never assumed important proportions. The largest numbers were reached after the activity of the three other groups had subsided, indicating that these organisms were better able to utilize the more resistant organic compounds in the straw than the other groups.

The repeated field applications of straw and nitrogen fertilizers did not affect  $\text{CO}_2$  evolution and microbial activity to any appreciable extent.

The water-soluble substances contributed by the straw were decomposed largely in 37 days. The bacteria, because of rapid increase and superiority in numbers, were responsible for the major part of this decomposition.

The hemicellulose and cellulose compounds decomposed at a uniform rate during a period of approximately 80 days. The bacteria and actinomycetes as well as the fungi took an important part in the decomposition of these products.

In the process of decomposition the protein content of the organic matter was steadily building up as a result of the rapid loss in carbohydrate materials and synthesis of protoplasm by the microbes.

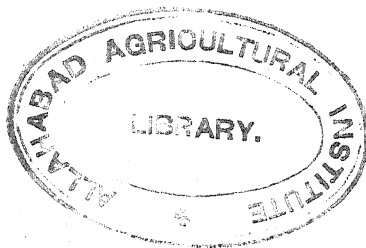
The relative amounts of lignin in the treated soils increased gradually, in-

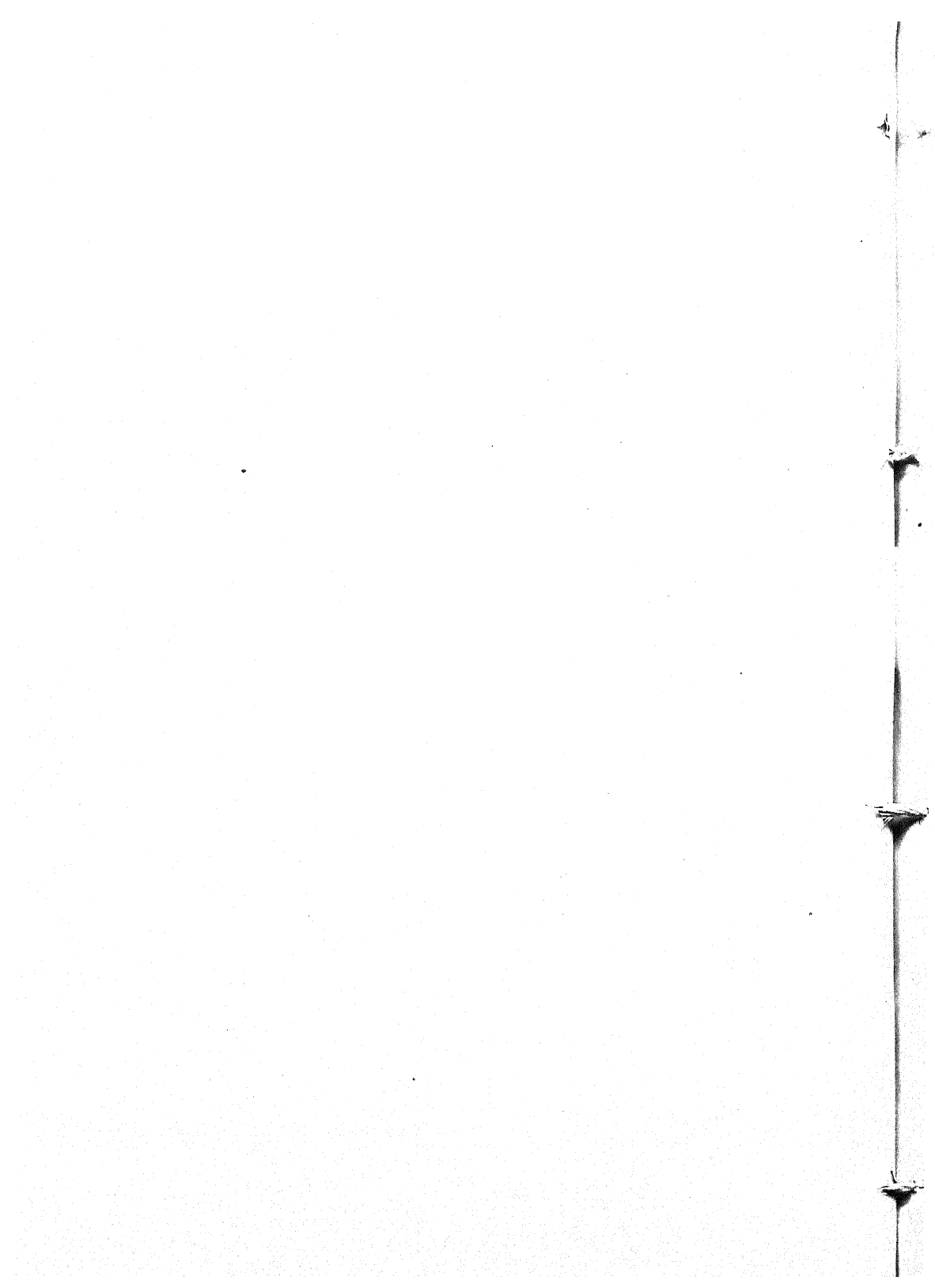


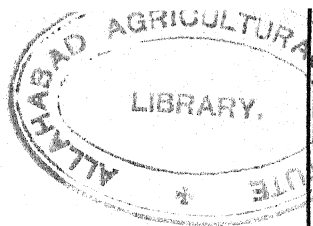
dicating that the major part of the lignin compounds supplied by the straw were not attacked by the microorganisms during the course of the experiment.

## REFERENCES

- (1) Association of Official Agricultural Chemists. 1930 Official and Tentative Methods of Analysis, ed. 3, p. 4-405. Washington, D. C.
- (2) FRED, E. B., AND WAKSMAN, S. A. 1928 Laboratory Manual of General Microbiology, p. 9. McGraw-Hill Book Co., Inc., New York.
- (3) FRIEDEMANN, T. C., AND KENDALL, A. I. 1929 The determination of carbon and carbon dioxide. *Jour. Biol. Chem.* 82: 45-55.
- (4) HECK, A. F. 1929 A study of the nature of nitrogenous compounds in fungus tissue and their decomposition in the soil. *Soil Sci.* 27: 1-49.
- (5) NORMAN, A. G. 1931 The biological decomposition of plant materials. IV. The biochemical activities on straw of some cellulose decomposing fungi. *Ann. Appl. Biol.* 18: 244-259.
- (6) TENNY, FLORENCE G., AND WAKSMAN, S. A. 1929 Composition of natural organic material and their decomposition in the soil: IV. The nature and rapidity of decomposition of the various organic complexes in different plant materials under aerobic conditions. *Soil Sci.* 28: 55-84.
- (7) VANDECAVEYE, S. C., AND ANDERSON, S. 1934 Longevity of *Azotobacter* in soils treated with lime and superphosphate. *Jour. Amer. Soc. Agron.* 26: 353-364.
- (8) VANDECAVEYE, S. C., AND VILLANUEVA, B. R. 1934 Microbial activity in soil: I. Nitrogen fixation by *Azotobacter* and activity of various groups of microbes in Palouse silt loam. *Soil Sci.* 38: 191-205.
- (9) WAKSMAN, S. A., AND SKINNER, C. C. 1926 Micro-organisms concerned in the decomposition of cellulose in the soil. *Jour. Bact.* 12: 57-84.
- (10) WAKSMAN, S. A., AND STEVENS, K. R. 1928 A critical study of the methods for determining the nature and abundance of soil organic matter. *Soil Sci.* 30: 97-117.
- (11) WAKSMAN, S. A., AND STARKEY, R. L. 1931 The soil and the Microbe, p. 215. John Wiley & Sons, New York.







There are nearly 4000 Institutions of pure and applied botany. There are between 60,000 and 70,000 botanists. There are about 1000 periodicals concerned with botany!

How can you keep in touch with all this activity? How can you find out what other botanists are doing and what new work they are planning?

CHRONICA BOTANICA will help you. Subscribe to it and help with the compilation of the next volume.

All directors of institutions and secretaries of societies will receive a copy of our questionnaire at the beginning of December of each year. Replies should reach the Editor-in-Chief, Dr. F. Verdoorn, Leiden, Holland not later than January 30th, as it will generally be impossible to make use of information received after that date. Directors or secretaries, who do not receive our preliminary circular, which will reach them annually before Oct. 15th, are kindly requested to acquaint us of the fact at their earliest convenience, which will enable us to include them in our mailing list, and will ensure their receiving a copy of the questionnaire in December.

Prospectus, sample pages and further information may be had from the Editorial and Publishing Office,  
P. O. Box 8, Leiden, Holland

## Second Edition WEATHER PROVERBS AND PARADOXES

By William J. Humphreys  
METEOROLOGICAL PHYSICIST, U. S. WEATHER BUREAU

*It EXPLAINS the Weather*

*It FORECASTS the Weather*

*It Makes one WEATHER WISE*

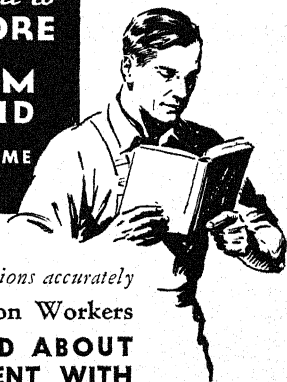
OF COURSE, it's not an almanac. But a reading does enable one to read the signs and have a good idea of what weather is 'being manufactured up there. Moreover, the whys and wherefores are stated. Nature's startling paradoxes are explained. The truth that is in old saws is brought out—the proverbs that are absurd are omitted.

*Sixteen half-tones and two graphs are included.*

**\$2.00**

THE WILLIAMS & WILKINS COMPANY  
BALTIMORE, U. S. A.

*Farmers want to*  
**KNOW MORE**  
*about*  
**CALCIUM**  
**CYANAMID**  
*the*  
**NITROGEN + LIME**  
**FERTILIZER**



*To answer their questions accurately*  
Experiment Station Workers  
**SHOULD READ ABOUT**  
**AND EXPERIMENT WITH**  
**'AERO' CYANAMID**

as a source of nitrogen and lime.

A bag of AERO Cyanamid will gladly be supplied, free of charge, to any reader of this Journal who desires to give the material a field trial.

Write **AMERICAN CYANAMID COMPANY**  
30 ROCKEFELLER PLAZA, NEW YORK



*Manufacturers of*  
**'AERO' CYANAMID — 'AMMO-PHOS'**

# Potash and Good Keeping Quality

**H**ARVESTS are over and fruits and vegetables have been put into storage. Scientific research indicates that potash plays an important part in their keeping qualities.

In the case of apples, work reported shows that potash-starved trees produced fruit in which there was a large percentage of spoilage from internal browning while in storage. There was no spoilage in the fruit from trees sufficiently fed with potash to balance the other plant-food elements.

Good produce is not profitable unless it maintains its quality until it reaches the ultimate consumer.

**AMERICAN POTASH INSTITUTE, INC.**  
Investment Building Washington, D. C.

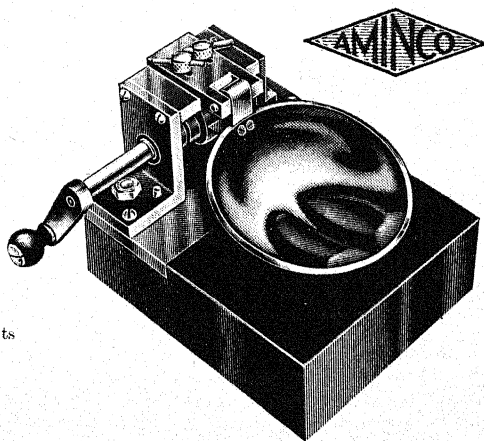
## SOIL-TESTING INSTRUMENTS

And Apparatus of All Kinds

We specialize in the manufacture of soil-testing instruments, after the designs of the U. S. Bureau of Chemistry and Soils, the U. S. Bureau of Public Roads, the A.S.T.M., the American Association of State Highway Officials, and others.

Following are some of the soil-testing instruments described in our catalog:

Soil Dispersion Apparatus  
Soil Sampling Tubes  
Plasticity Apparatus  
Soil Compression Device  
Shrinkage Factor Apparatus  
Bouyoucos Hydrometers  
Soil Centrifuges



Above: Liquid Limit Device, after the design of the Bureau of Public Roads

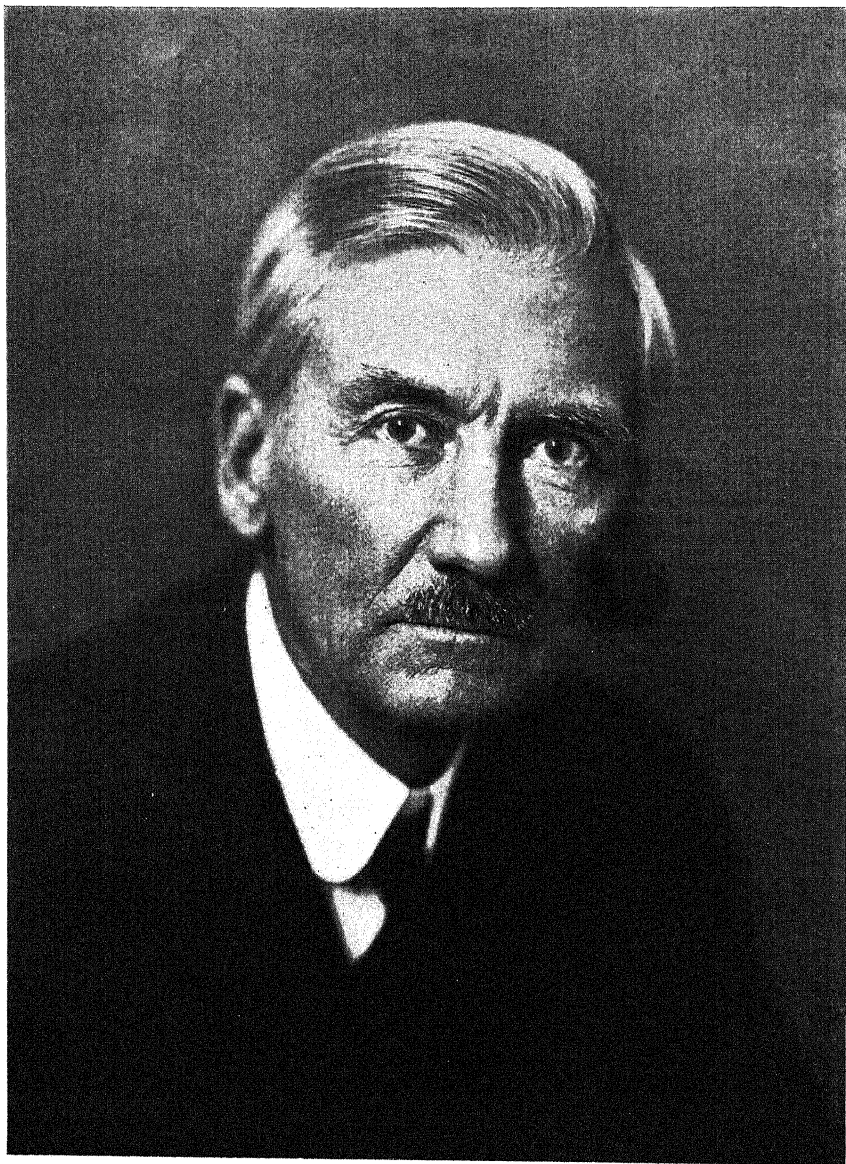
*Write for the Aminco Catalog*

**AMERICAN INSTRUMENT COMPANY, INC.**

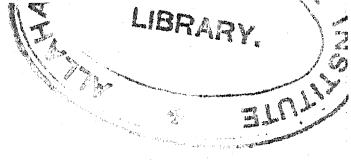
774-776 Girard Street, N.W.

Washington, D. C.





CURTIS F. MARBUT



## Curtis F. Marbut

1863-1935

One of the world's greatest authorities on soils, Dr. Curtis F. Marbut, for many years Chief of the Soil Survey of the United States Department of Agriculture, died in Harbin, Manchuria, August 25. At the time of his death, he was on his way to make a study of the soils of China at the request of the Chinese Government.

Doctor Marbut, who had passed the age of retirement, had been retained by the United States Government for two additional years in order to continue exceptionally important research on the classification of soils in this and other countries.

For twenty-five years Doctor Marbut had supervision of the soil survey work of the United States Department of Agriculture, which has mapped approximately one billion acres of land, or about half the agricultural area of the United States. He recently finished the first complete inventory of the soil resources of the entire nation. This volume, soon to be published by the United States Department of Agriculture as part three of its *Atlas of American Agriculture*, contains the information accumulated during his supervision of the Soil Survey, and its mapping and description of the soils of 1,500 counties and areas in the United States and its insular possessions. As a guide to farm practice, this inventory of soil resources is becoming established as one of the most important parts in the scientific foundation of this country's agricultural program.

Not only did Doctor Marbut know the soils of the United States, but he had examined and classified the soils in every country of western Europe, except Spain. He was familiar with the soils of Russia, had directed the classification of the soils of Africa, and had made a study of the soils of South America.

In recognition of his extensive studies and classification of soils, which have furnished an important contribution to the soil geography of the world, Doctor Marbut was awarded the Cullum Geographical Medal in 1930, "for services of special distinction in the field of exploration and geographic research." He received the degree of doctor of laws from the University of Missouri, from which he was graduated in 1889, and where he was formerly professor of geology. He also received the degree of doctor of science from Rutgers University. He was chairman of the International Commission on Genesis, Classification, Morphology, and Mapping of Soils and was president of Commission V on Soil Classification at the Third International Congress of Soil Science at Oxford, England, where during the first week of August he presided over important discussions by members of the congress from all parts of the world. Doctor Marbut was a member of many learned societies. He was born in Lawrence County, Missouri, July 19, 1863.





# CHEMICAL NATURE OF ORGANIC MATTER IN DIFFERENT SOIL TYPES<sup>1</sup>

SELMAN A. WAKSMAN AND I. J. HUTCHINGS<sup>2</sup>

*New Jersey Agricultural Experiment Station*

Received for publication January 3, 1935

A systematic study of the proximate chemical composition of the organic matter or humus in composts (19), peats (21), and the upper layers of forest soils (23) represents comparatively little difficulty, largely because of the fact that these formations are predominantly organic in nature. One can readily establish the relation between the specific chemical constituents of these types of humus and the corresponding compounds in the plant residues from which these humus formations originated. The study of humus in soil horizons which are predominantly inorganic in nature, however, represents a number of highly confusing problems. The great majority of investigations carried out with this type of humus were based upon preparations obtained from mineral soils by means of strong chemical reagents, which resulted in considerable changes in the chemical nature of the humus. There was still less justification for applying data obtained from the study of humus in peats and even coals to an understanding of the chemical composition of humus in field and garden soils. The chemistry of humus in mineral soils, its function, and its transformations still represent a number of unsolved problems which are among the most important in soil science.

The very conception of humus has recently been subjected to considerable criticism. Sufficient emphasis has already been laid (16, 17) upon the fact that humus is not—1, the alkali-soluble portion of the soil organic matter; nor 2, the alkali-soluble and acid-precipitated portion; nor 3, that fraction of the soil which is oxidized by dilute  $H_2O_2$  or by other mild oxidizing agents; nor 4, the acetyl-bromide insoluble portion; nor 5, any other fraction of the organic matter. It represents the total organic matter of the soil and must be considered as such. It has been definitely established that humus does not consist of a few simple compounds, the so-called humic acids, to which various hypothetical formulas have been ascribed, but that it is highly complex in chemical composition. It has been further suggested (16, 22) that

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

<sup>2</sup> The authors are indebted to Prof. A. W. Blair, to Dr. Marbut, and to Dr. Shaw, for supplying samples of soil, and to Dr. M. C. Allen, formerly of this laboratory, for assistance in some of the analyses.

humus be divided, by the method of proximate analysis, into several groups of organic complexes possessing definite chemical properties and having their corresponding constituents in plant residues.

The study of humus in mineral soils presents a number of problems dealing, aside from its chemical nature, also with its formation; transformation by microorganisms and chemical agencies; functions in soil processes, especially its relation to the physical and chemical properties of the soil; and soil fertility. Most significant of these are two problems, based upon the quantitative and qualitative composition of humus, which involve a study of methods for determining the abundance and chemical nature of humus in mineral soils. These form the subject of this paper.

#### QUANTITATIVE DETERMINATION OF ORGANIC MATTER IN MINERAL SOILS

The more important methods proposed at different times for determining the organic matter content of mineral soils can be divided into the following four groups: 1. loss on ignition, directly, or after preliminary treatment of the soil with certain chemical reagents so as to remove those mineral complexes which may also give a loss on ignition; 2. complete combustion of the organic matter and calculation of the total humus from the organic carbon content, by the use of a certain arbitrary factor; 3. oxidation of humus by means of strong oxidizing agents; 4. miscellaneous other methods, such as calculation of humus from the total nitrogen in the soil and the distillation method. A number of methods have also been proposed for determining the abundance in soil of certain humus fractions, usually designated as the "humified" portions of the soil organic matter. The assumption was thereby made that plant and animal substances, in the process of their decomposition, change first into humus before they become completely mineralized. Aside from the lack of validity for any such assumption, these methods need not be discussed here further, since they have only a limited bearing upon the problem under consideration.

*Ignition methods.*—It has been definitely agreed that the loss-on-ignition method cannot be recommended for determining accurately the organic matter content of mineral soils. The error involved by the use of this procedure is too large to make the results more than highly proximate in nature. This method was modified by Rather (8), who suggested treatment of the soil, previous to ignition, with a mixture of dilute hydrochloric and hydrofluoric acids. This modification suffers from certain distinct disadvantages: 1. some of the constituents of the humus, such as the uronic acid complexes, tend to be destroyed during the preliminary treatment of the soil, while other humus fractions may be brought into solution; 2. the method is time consuming (1); 3. at best, the results thus obtained are only indirect.

*Combustion methods.*—The complete oxidation of the soil organic matter, whether by dry or wet combustion methods, has been used most extensively.

It is now generally agreed that the determination of the total organic carbon in soil is the most accurate method available, at the present time, for determining the humus content. However, certain difficulties arise in interpreting the results thus obtained, chief among which is the specific factor to be used for calculating the humus from the carbon data. Fresh plant residues contain about 50 per cent carbon, thus giving a ratio of organic matter (a very low ash content being assumed) to carbon of about 2:1. When these residues are allowed to undergo decomposition by microorganisms in soils or in composts, the carbon content of the resulting humus becomes gradually higher, but never above 60 per cent unless the residues become fossilized. This is due to the fact that the carbohydrate constituents of the plants, namely, the sugars, polyuronides, hemicelluloses, and cellulose, which have a carbon content of 38 to 43 per cent, are among the first to decompose and disappear from the humus. On the other hand, the lignin, with a carbon content of 62-64 per cent is more resistant to decomposition and, therefore, accumulates. The proteins with a carbon content of 50-52 per cent also tend to persist in the humus and even accumulate.

The carbon content of the humus which results from the decomposition of the plant and animal residues depends largely upon the extent of their decomposition. In the case of the upper layers of a raw humus forest soil or of a highmoor peat bog, the carbon content increases only little, perhaps only to 52 or 54 per cent, because of the persistence of a large part of the carbohydrates. When humus is at that stage of decomposition when most of the cellulose and hemicelluloses have disappeared, the carbon content will have increased to 56 and even 58 per cent, as is the case in mineral soils, lowmoor and sedimentary peats, and the lower horizons of forest soils. This bears out fully the earlier ideas of Wolff (26), van Bemmelen (2), and others who assumed that the carbon content of humus is 58 per cent and that the factor to be used for calculating the amount of humus in mineral soils should be 1.724. In the case of the humus horizons of forest (7), heath, and alpine soils, however, this factor has to be modified, since the humus in these soils contains a considerable amount of cellulose and hemicelluloses; in the case of the upper layers of forest soils, peat bogs, and peat soils, the determination of the organic matter content by the loss on ignition is frequently justified.

*Oxidation methods.*—Among the various oxidation methods, that of Robinson (10), which consists in the treatment of soil with 15 to 30 per cent hydrogen peroxide, deserves particular attention; however, this method as well has been shown (1) to be far from satisfactory. The permanganate method of Istsherikov, the sodium peroxide method of Parr, and other oxidation procedures are also open to criticism, on various grounds which need not be discussed here.

Among the rapid methods of humus determination in soil, the Schollenberger (12) procedure or one of its modifications (15) deserves careful consideration.

The results obtained by this method check very well with those obtained by complete combustion, even in the case of soils of a very low organic matter content.

*Other methods.*—In many cases, the humus content of the soil was calculated from the total nitrogen, as determined by the Kjeldahl method. The relation between organic matter and nitrogen was usually assumed to be 20:1. This method meets with even more serious objections; it involves not only the use of an arbitrary factor, which may vary considerably for different humus formations, but it also assumes a constant relation between the carbon and nitrogen content of the humus. This method as well cannot, therefore, be recommended.

TABLE 1

*Organic matter content of a series of soils, as determined by different methods*  
Per cent of air-dry material

NAME OF SOIL	ORGANIC MATTER BY DISTILLA- TION METHOD*	CARBON CONTENT BY COMBUS- TION METHOD	CARBON BY OXIDATION METHOD (MODIFICA- TION OF SCHOLLEN- BERGER METHOD)	ORGANIC MATTER BY COMBUS- TION METHOD (C × 1.724)	NITROGEN CONTENT
Michigan podzol, 3.5–5 cm.....	33.19	24.11	25.26	41.47	1.07
Michigan podzol, 5–20 cm.....	0.71	0.65	0.64	1.12	0.052
Tchernozem soil, Texhoma, Okla., 0–20 cm.....	1.43	0.78	0.82	1.41	0.086
Tchernozem soil, Texhoma, Okla., 20–50 cm.....	1.31	0.60	0.64	1.10	0.073
Chestnut soil, N. M. 0–18 cm.....	1.08	0.95	1.09	1.93	0.101
Serozem, Ariz., 0–15 cm.....	0.37	0.16	0.16	0.28	0.023
Colbert clay, 0–15 cm.....	0.50	0.67	0.64	1.16	0.048
Hagerstown clay, 50–75 cm.....	0	0.18	0.31	0.31	0.037
Stockton adobe, 0–40 cm.....	0.40	0.53	0.60	0.91	0.051
Irredell loam, 30–40 cm.....	0.26	0.30	0.38	0.52	0.042
Marion silt loam, surface.....	2.44	1.80	1.70	3.10	0.170

\* Analyses made by Dr. Bouyoucos.

Bouyoucos (4) suggested that the organic matter content of the soil be calculated by determining both the loss on ignition and the amount of chemically combined water. Air-dried soil was heated at a high temperature and the liberated water condensed; the weight of this water was subtracted from the loss on ignition, to give the amount of organic matter present. This method has no advantage over the other methods already referred to, especially since it is more complicated and less direct. The organic matter in a series of soils analyzed by Bouyoucos was compared with the amount of humus found in these soils by the combustion method (table 1). The distillation procedure gave in most cases too low results, frequently less than a half of the organic matter content of the soil, as calculated from the organic carbon.

A comparison of the different methods for the determination of humus in mineral soils can lead to only one conclusion, namely, that the only reliable method available at the present time is that based upon the organic carbon content. All other methods are either proximate in nature or more complicated, and usually less reliable. The major difficulty involved in the use of this method is the nature of the factor used in calculating the humus. Because of the undisputed fact that the carbon content of the organic matter in composts, peat bogs, and mineral soils varies, depending on the extent of its decomposition, the use of any one factor has frequently been questioned. It has even been suggested (7) that different factors be used for different types of humus. However, since even one type of humus varies considerably, depending on a number of factors, especially the nature of the residues undergoing decomposition, the mineral part of the soil, the type of decomposition, and the extent of decomposition, one has to exercise special precautions in recommending the use of several factors. If any multiplicity of factors is to be recommended, the following deserve consideration:

The factor 1.724, proposed by Wolff and used extensively by soil chemists and geneticists, for mineral soils.

The factor 1.862, for lowmoor and sedimentary peats and for the F and H layers of raw-humus forest and heath soils.

The factor 2.0 for composts, highmoor or sphagnum peats, and litter of forest soils.

If the mineral content of a particular soil layer, such as the organic layers of forest soils, or of other humus formation, such as peats and composts, is less than 10 per cent, the loss on ignition is as reliable as the foregoing method of calculation.

#### CHEMICAL NATURE OF HUMUS IN MINERAL SOILS

Three distinctly different methods of approach have been utilized for the study of the chemical nature of humus in mineral soils: 1. The separation of the humus into several groups of complexes by extraction with dilute alkali solutions and precipitation with acids; whatever justification the study of "humic acids," "humic matter," or "pure humus" may have had from the point of view of the presence in the soil of certain characteristic dark colored, amorphous bodies, high in carbon, it has contributed comparatively little toward an understanding of the chemistry of humus as a whole, its origin, and its rôle in soil processes. 2. The isolation from soil of well-defined chemical compounds of an organic nature; the information thus gained has been of considerable importance for a better understanding of the origin and occurrence of specific complexes in the soil, but it has not explained the chemical nature of humus as a whole. 3. The proximate chemical analysis of humus; just as in the case of natural formations predominantly organic in nature, such as peats and organic layers of forest soils, the humus of mineral soils can be

subdivided into several fractions, characterized by specific chemical properties, which have their counterpart in the plant residues (16, 22).

The proximate method of analysis of humus in mineral soils has now been carried out in various laboratories, so that sufficient evidence has accumulated to determine the extent to which it can be utilized for the study of the organic chemistry of the soil. Unfortunately, certain discrepancies have frequently been introduced by some workers who have attempted to use this method; attention must be called to some of these here. Briefly, the analysis is carried out as follows: one hundred to one thousand gram portions of air-dried soil are treated thoroughly with (a) ether, (b) hot alcohol, (c) hot water, (d) hot 2 per cent HCl solution, and (e) 80 per cent sulfuric acid in the cold. There is little difficulty in determining the amount and nature of the organic matter fractions in the first three extractions. The fraction hydrolyzed by the dilute mineral acid needs further elucidation. The hemicelluloses form the major group of organic constituents of the humus hydrolyzed or brought into solution by this treatment; the total amount of hemicelluloses can be calculated from the reducing substance found in the extract, after the latter has been neutralized with an alkali solution and the inorganic precipitate has been removed by filtration. However, polyuronides are present abundantly in humus; they are also hydrolyzed to a large extent by the dilute acid treatment but are only partly transformed into reducing bodies; the total amount of reducing sugar obtained does not represent, therefore, all the hemicelluloses, including the polyuronides present in the humus. This is largely the reason why the hemicellulose content of humus in mineral soils, especially in gray desert soils, has frequently been reported as too low; this fraction was found abundantly only in the organic layers of podzols, in peats, and in composts. Because of the small amount of reducing sugar found in the dilute acid hydrolyzate of mineral soils and because of the difficulty of determining reducing sugar in low concentrations, some investigators (5) analyzed the hydrolyzate for total carbon and calculated the whole fraction as hemicellulose; the error thus introduced is very large and totally unjustified. A large part of the organic matter in the acid extract is due to hydrolyzed proteins; some is due to lignin, as well as to other complexes brought into solution by the acid; only a part of the hydrolyzate is due to true hemicelluloses. The only justified term for this mixed fraction is "dilute acid hydrolyzable organic fraction;" the hydrolyzed protein must, however, be accounted for, if the protein is reported separately. After hydrolysis with dilute mineral acid, the soil is washed with water and dried, and definite portions (10-15 gm.) are treated with 80 per cent sulfuric acid for the determination of the cellulose and lignin fractions.

This system of analysis can be utilized in numerous investigations of the chemical nature of humus. It is sufficient to mention the study of the degree of decomposition of the humus, especially in peats and in composts. In the case of humus in mineral soils, it can find special application in the study of the influence of soil treatment in modifying the nature of the humus, and in the study of humus in different soil types and in the different horizons of the same soil type.

*Influence of soil treatment upon the chemical composition of the humus.* For this study, a series of plot and cylinder experiments at the College Farm of the New Jersey Agricultural Experiment Station have been utilized. The special treatment of the plots was carried out for a period of 25 years, so that marked differences were brought about in the chemical nature of the soil as a whole and of the humus content in particular. The cylinder experiments were of shorter duration, hence the modifications of the humus are not so striking.

The results presented in tables 2 and 3 show that the humus content of a given soil type can be considerably modified by treatment; however, the general chemical nature of the humus in the soil tends to be the same. Treatment of the soil plots with stable manure for a period of 25 years resulted in a considerable increase in the humus content, without modifying to any great extent its chemical nature. Liming of the soil brought about a decrease in the ether-soluble fraction and an increase in the water-soluble fraction, but not of the other humus constituents. In the cylinder experiments, the increasing addition of straw resulted in a gradual increase in humus content.

TABLE 2

*Influence of soil treatment upon the chemical nature of humus in a mineral soil\**

PLOT NUMBER.....	7A	5A	19A	7B	5B	19B
TREATMENT†.....	Untreated	Manure + minerals	Minerals only	Lime	Manure + lime + minerals	Lime + minerals
<i>Per cent of dry material</i>						
pH.....	4.6	5.2	5.0	7.4	7.1	7.3
C:N.....	10.5	11.7	11.2	10.5	10.4	10.8
Organic matter ( $C \times 1.72$ ).....	1.41	3.01	1.96	1.74	2.94	1.63
Total nitrogen.....	0.078	0.149	0.102	0.096	0.165	0.088
<i>Per cent of total humus</i>						
Ether-soluble portion.....	5.67	1.53	6.89	0.74	0.82	3.61
Alcohol-soluble portion.....	1.78	1.57	1.84	1.84	1.49	2.70
Cold- and hot-water-soluble portions.....	1.84	2.50	2.35	3.58	4.42	3.87
Hemicelluloses.....	7.19	7.87	7.48	6.05	8.39	6.91
Cellulose.....	3.64	3.15	2.43	2.45	3.80	2.60
Lignin.....	34.90	42.20	30.03	34.52	40.71	38.87
Protein.....	34.61	31.03	32.55	34.48	35.07	33.74
Total accounted for.....	89.61	89.85	83.57	83.66	94.70	92.30

\* Sassafrass loam.

† A detailed discussion of the treatment of these plots for a period of 25 years and crop yields are given by Lipman and Blair (6).

The most important modification of the humus was the gradual decrease in protein content, which, in the case of the soil receiving nitrogen, became marked only with the largest additions of straw. Accompanying the decrease of protein, there was a gradual increase in cellulose. Before any general conclusions are drawn from these experiments, a greater number of analyses will have to be made than was so far possible.

*Chemical composition of humus in podzols.* The rôle of humus in the process of podzolization is well established and need not be discussed here further. However, although it is known that humus is removed from the A horizon

TABLE 3  
Influence of increasing additions of straw upon the organic matter content of the soil\*

CYLINDER NO.	121-2†	123-4	125-6	127-8	129-30	131-2	133-4	135-6	137-8	139-140
STRAW ADDED TONS PER ACRE	0	1	2	4	8	0	1	2	4	8
<i>Per cent of dry material</i>										
Organic matter ( $C \times 1.724$ )	2.29	2.36	2.47	2.69	3.26	2.21	2.26	2.40	2.45	3.07
Total nitrogen	0.099	0.102	0.104	0.111	0.126	0.097	0.097	0.107	0.107	0.119
C:N	13.4	13.4	13.6	14.1	15.0	13.2	13.5	13.0	13.3	15.0
Increase in organic matter due to treatment, per cent.	.....	3.1	7.9	17.5	42.4	.....	2.3	8.6	10.9	38.9
<i>Per cent of total humus</i>										
Ether-soluble portion	1.2	1.1	1.1	1.2	1.2	1.5	1.4	1.4	1.3	1.4
Alcohol-soluble portion	1.2	1.3	1.3	1.0	0.8	0.7	0.8	0.9	0.9	0.9
Hot-water-soluble portion	1.6	0.9	1.0	0.8	1.2	1.6	1.2	1.1	1.3	1.1
Hemicelluloses	5.2	4.9	5.6	6.0	5.8	3.9	4.3	4.6	5.3	4.5
Cellulose	2.3	3.2	3.6	4.2	3.7	2.4	3.0	2.3	3.7	4.3
Lignin	51.3	50.5	41.9	47.1	57.7	50.8	49.7	43.0	44.3	53.7
Protein	27.0	27.0	26.3	25.8	24.2	27.4	26.8	27.9	27.3	24.2
Total accounted for	89.8	88.9	80.8	86.1	94.6	88.3	87.2	81.2	84.1	90.1

\* A detailed discussion of the treatment of these cylinders for a period of 10 years is given by Blair and Prince (3).

† Cylinders 121-130 received, at irregular intervals, extra applications of nitrogen as  $\text{NaNO}_3$ , although cylinders 131-140, as well, had leguminous crops and some nitrogen application.



and is reprecipitated in the B horizon, it still remains to be determined whether this removal takes place at the expense of the humus as a whole or of only certain specific humus constituents. The fact that the nitrogen content of the humus was often found to increase with depth of profile suggests that the latter assumption is justified. It is sufficient to call attention, among the recent investigations, to the work of Weis (25). The following amounts of humus and total nitrogen were found on an average of 10 profiles of Danish heath soils:

HORIZON	HUMUS CONTENT OF SOIL	NITROGEN CONTENT OF SOIL	NITROGEN IN HUMUS
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Raw humus (A <sub>1</sub> ).....	27.03 (7.98-51.73)	0.49 (0.14 -1.06)	1.81
Bleached sand (A <sub>2</sub> ).....	1.78 (1.05- 2.94)	0.03 (0.02 -0.04)	1.69
Humus hardpan (A <sub>3</sub> -B <sub>1</sub> ).....	12.65 (9.85-16.17)	0.29 (0.21 -0.39)	2.29
Iron hardpan (B <sub>2</sub> ).....	2.65 (1.31- 4.66)	0.06 (0.03 -0.10)	2.27
Subsoil (C).....	0.24 (0.11- 0.81)	0.005 (0.003-0.016)	2.08

Even larger increases in the relative nitrogen content of the humus, with an increase in depth, were reported in some of his earlier analyses of the profiles of the hill islands and heath plains of Denmark (24).

In order to determine whether there is any difference in the chemical nature of the humus in the various horizons of the podzol profile, the results of analyses of three profiles are reported here (tables 4-6).

The first profile was obtained from a virgin heath on the Clason estate in Jutland, during the summer of 1933. The sample of the A<sub>1</sub> horizon was taken at a depth of 5-8 cm., just below the vegetation layer; that of the A<sub>2</sub> horizon, at a depth of 12-15 cm.; and that of the B horizon, at a depth of 30 cm.

The proximate method of analysis has been modified in the case of these profiles in one important respect. It was found that on treating the material with hot dilute HCl, to determine the hemicelluloses, as well as in the sulfuric acid treatment for the cellulose determination, a considerable amount of the lignin passes through the paper in the water used for washing the hydrolyzed residue; this held true for all the podzol horizons, but especially for the B horizon. The lignin fraction of the humus in this horizon was so mobile that nearly two-thirds of it was removed in the wash water following the acid treatments. In order to account for this lignin, the filtrates were analyzed for total organic carbon; the carbon equivalent of the hemicellulose and cellulose found in the extracts and the carbon equivalent of the hydrolyzed protein were subtracted and the rest of the carbon was calculated as lignin.

The second podzol profile was supplied by Doctor Marbut of the U. S. Department of Agriculture. It represents a trenary sandy loam, from Alge Co., Michigan. Only the A<sub>1</sub> and A<sub>2</sub> horizons of this profile were available, the A<sub>1</sub> being taken at 3-5 cm. and A<sub>2</sub> at 5-20 cm. depth.

The third profile was obtained from a raw-humus forest soil, in a white pine-hemlock forest, at Keene, New Hampshire.

The three podzol profiles varied markedly from one another. Although the first two profiles contained nearly the same amounts of organic matter in the A<sub>1</sub> and A<sub>2</sub> horizons, the nature of this organic matter was quite different. The humus in the heath profile was lower in nitrogen than that of the Michigan podzol, as a result of which the C:N ratio was much wider in the former. The humus in both profiles was high in cellulose, hemicellulose, and lignin in the A<sub>1</sub> horizon; these diminished gradually in the A<sub>2</sub> horizon, accompanied by an increase in the protein content. The ether-soluble substances were high in the heath and low in the Michigan profile; there was an increase in concen-

TABLE 4  
*Chemical composition of humus in a heath podzol*

HORIZON	A <sub>1</sub>	A <sub>2</sub>	B
<i>Per cent of dry material</i>			
Total humus ( $C \times 1.724$ ).....	38.70	1.22	2.99
Total nitrogen.....	0.54	0.019	0.048
C:N.....	41.7	37.4	36.3
Nitrogen in humus.....	1.395	1.557	1.605
<i>Per cent of humus</i>			
Ether-soluble portion.....	3.77	13.93	1.32
Alcohol-soluble portion.....	4.03	3.52	2.75
Cold- and hot-water-soluble portions.....	0.59	1.14	0.58
Hemicelluloses (sugar $\times 0.9$ ).....	14.25	5.90	8.12
Cellulose (sugar $\times 0.9$ ).....	14.81	5.41	3.12
Lignin, nitrogen-free.....	50.85	45.74	63.14
Protein.....	8.71	9.75	10.03
Total accounted for.....	97.01	85.29	89.06

tration of this fraction from the A<sub>1</sub> to the A<sub>2</sub> horizon, followed by a rapid drop in the B horizon. The results obtained for the third profile were similar to those for the first two profiles. In this case, the litter and A<sub>0</sub> were also analyzed. With an increase in depth, the litter was gradually transformed into typical humus. This process of transformation was characterized by a gradual decrease in the ether-soluble material, in the hemicelluloses, and in the cellulose, and by an increase in the lignin and protein content.

Although the results of these analyses permit certain generalizations concerning the chemical nature of humus in the podzol profile, they are not sufficient to justify any broad conclusions, because of the important differences in the nature of the profiles. Weis also obtained considerable variation in the chemical composition of different heath podzols, as shown by the variation in nitrogen content and in the C:N ratio.

TABLE 5  
*Chemical composition of humus in a Michigan podzol*

HORIZON	A <sub>1</sub>	A <sub>2</sub>
<i>Per cent of dry material</i>		
pH.....	4.59	5.13
Total humus ( $C \times 1.724$ ).....	41.57	1.10
Total nitrogen.....	1.07	0.052
C:N.....	22.5	12.4
Nitrogen in humus.....	2.574	4.727
<i>Per cent of humus</i>		
Ether-soluble portion.....	0.97	2.90
Alcohol-soluble portion.....	2.32	1.68
Cold- and hot-water-soluble portions.....	4.00	6.36
Hemicelluloses (sugar $\times 0.9$ ).....	11.54	8.18
Cellulose (sugar $\times 0.9$ ).....	5.00	2.10
Lignin, nitrogen-free.....	55.62	46.32
Protein.....	16.08	27.82
Total accounted for.....	95.53	95.36

TABLE 6  
*Chemical composition of humus in a raw-humus forest podzol*

HORIZON	LITTER	F-LAYER	H-LAYER	A <sub>1</sub>	A <sub>2</sub>	B <sub>1</sub>	B <sub>2</sub> -C
<i>Per cent of dry material</i>							
pH.....	4.5	4.2	3.8	4.0	4.0	4.2	4.3
Loss on ignition, per cent.....	96.00	82.04	75.20	18.95	5.80	11.75	9.90
C:N.....	59.5	24.7	26.6	24.6	16.3	18.3	21.8
Organic matter, ( $C \times \text{factor}$ )*..	96.17	78.19	74.20	18.46	4.33	8.36	5.94
Total nitrogen.....	0.84	1.75	1.56	0.42	0.15	0.26	0.15
Nitrogen in humus.....	0.87	2.24	2.10	2.28	3.46	3.11	2.53
<i>Per cent of humus</i>							
Ether-soluble portion.....	6.38	4.86	4.25	3.21	3.12	1.54	1.00
Alcohol-soluble portion.....	2.57	4.16	3.54	2.25	2.42	1.08	0.98
Cold- and hot-water-soluble portions.....	4.06	6.73	3.31	1.88	4.10	2.38	1.03
Hemicelluloses.....	18.23	11.94	9.49	8.00	10.30	8.70	6.22
Cellulose.....	15.72	8.24	4.75	.....	.....	.....	.....
Lignin.....	38.38	44.24	50.13	.....	.....	.....	.....
Protein.....	5.44	14.00	13.12	14.25	21.50	19.43	15.81
Total accounted for.....	91.65	90.17	85.22	.....	.....	.....	.....

\* The factor used for this calculation was  $(1.684 + 0.004 \times C:N)$ .

*Chemical composition of humus in tchernozems.* The transition of the podzols to the tchernozems is a result of a number of factors, chief among which is the change in climate from the cooler to the warmer regions, a decrease in humidity and rainfall, and a change in type of vegetation. These changes are principally responsible for the difference in the chemical nature of the humus in the two soil types; this is specifically due to (a) differences in the chemical composition of the plant residues, (b) differences in the physical and chemical soil conditions, (c) the specific microbiological population. The abundance of bases (calcium and magnesium) in the tchernozem soil brings

TABLE 7  
*Chemical composition of the humus in tchernozem soils*

NATURE OF SOIL	TEX- HOMA, OKLA- HOMA	TEX- HOMA, OKLA- HOMA	AMARILLO, TEXAS	TUANAH, TEXAS	
<i>Per cent of dry material</i>					
Depth, <i>cm.</i> .....	0-20	20-50	Surface	0-20	30-50
pH of soil.....	6.82	7.01	6.85	7.70	8.05
Total humus (C × 1.724).....	1.41	1.10	2.29	2.06	1.58
Total nitrogen.....	0.086	0.073	0.130	0.149	0.102
C:N.....	9.5:1	8.8:1	10.2:1	8.0:1	9.0:1
Nitrogen in humus.....	6.100	6.636	5.677	7.23	6.45
<i>Per cent of humus</i>					
Ether-soluble portion.....	1.70	3.14	1.57	2.02	2.47
Alcohol-soluble portion.....	0.90	0.86	0.46	0.74	0.69
Cold- and hot-water-soluble portions.....	2.76	2.36	2.36	1.32*	0.87*
Hemicelluloses.....	6.95	3.45	6.72	1.41	0
Cellulose.....	8.86	4.23	7.16	5.44	4.28
Lignin.....	32.59	35.26	35.81	35.36	32.53
Protein.....	38.08	41.45	35.50	44.34	32.53
Total accounted for.....	91.84	90.75	89.58	90.63	80.84

\* Cold-water-soluble only.

about a fixation of the humus which is produced in the decomposition of the plant residues. One would, therefore, expect that a transition from the podzols to the tchernozems should result, not so much in a change in the amount of humus found in these soil types, but rather in a change in its chemical nature.

Remezov (10) found the widest carbon-nitrogen ratio (10:1 to 14:1) in the humus of the tchernozems; this was explained by the higher lignin content, which was 2 to 2.5 times as high as the protein in the humus. These results would seem to conflict with those reported from this laboratory (16), namely, that the humus in tchernozems contains about 41 to 49 per cent lignin-like material and 30 to 35 per cent protein. Remezov, however, subtracted the

nitrogen found in the humus in the form of amides and amino acids from the total nitrogen and calculated the differences as protein, whereas the writer based the calculation of the protein upon the total organic nitrogen. Otherwise, the composition of the humus in the two groups of tchernozems is similar, as regards both protein and lignin concentration.

The results of analyses of three tchernozems—one from Texhoma, Oklahoma; one representing an Amarillo silty clay loam from Texas; and one from Tuanah, Texas—are given in table 7. A very decided difference was found in the chemical nature of the humus in these soils from that in the podzols. The humus in the tchernozems was characterized by a lower lignin and a higher protein content, a much lower hemicellulose and cellulose content, and a narrower C:N ratio. The organic matter in the podzols was not sufficiently decomposed, as shown by the high cellulose and hemicellulose content. This also accounts for the low nitrogen concentration in the humus of the podzols; the lignin seems to accumulate in the humus of these soils, whereas the protein does not accumulate or is partly removed. In the case of the tchernozems, the greater degree of decomposition of the humus, as shown by the low cellulose and hemicellulose content, resulted in a more extensive synthesis of protein; the latter became fixed by the lignin, in the presence of sufficient bases.

The results presented here fully confirm those obtained by Remezov (10) for the humus in the tchernozems; however, they are in total disagreement when the podzols are compared. Possibly, Remezov used, not virgin soils, but cultivated podzols, in which considerable disintegration of some of the humus constituents has taken place.

*Chemical composition of humus in chestnut soils and serozems.* The narrowest C:N ratio has usually been reported (9) for the humus of serozems (4.5:1), followed by that of the chestnut soils (6.8:1). This was explained by the fact that under the specific conditions of formation of these soils (dry continental climate, hot summer temperature, continuous winds, intensive evaporation and drying of soil), the limited vegetation yields a small amount of residual material which is rapidly decomposed. As a result of this, the humus content of the serozems (0.5–1.5 per cent) is low in spite of the old age of these soils. The humus of serozems was further characterized (10) by a complete absence of both cellulose and hemicelluloses and by a high protein content; the former was ascribed to the extensive decomposition of the plant residues in these soils and the latter to the fact that this humus is chiefly of microbial origin. The low content of lignin complexes was believed to be responsible for the low concentration of absorbed cations and the lack of structure in these soils. Humus in chestnut soils was also characterized by a lack of cellulose but it was high in hemicellulose; the lignin content was greater and the protein content lower than in the previous group of soils.

In the analyses reported here, two serozems and one chestnut soil were used. The latter came from New Mexico, 32 miles south of Tucumcari, and the former came from the Mohave desert, near Tucson, Arizona, and from

the Imperial Valley, California. The results (table 8) show that humus in chestnut soils is very similar in chemical composition to that of tchernozems, especially the humus in the Amarilla soil; the latter can actually be classified as a chestnut soil. There is no marked distinction in chemical composition of the humus in the two soil types, as found by Remezov; there is no abnormally high hemicellulose content in the chestnut soil, and the protein and lignin contents are similar in both soils. Perhaps the difference in the two sets of results is due to a lack of sharp distinction between the two soil types.

The humus in the serozems is quite characteristic. It has a narrow carbon-nitrogen ratio, much narrower than in the other soil types discussed in the

TABLE 8  
*Chemical composition of the humus in chestnut soil and serozems*

NATURE OF SOIL	CHESTNUT	CHESTNUT	ARIZONA SEROZEM	IMPERIAL SEROZEM
<i>Per cent of dry material</i>				
Depth, cm.....	0-15	15-48	0-15	0-15
pH of soil.....	6.82	7.01	7.21	8.38
Total humus (C $\times$ 1.724).....	1.93	1.31	0.28	0.066
Total nitrogen.....	0.101	0.076	0.0225	0.0064
C:N.....	11.1:1	10.0:1	6.4:1	6.0:1
Nitrogen in humus.....	5.233	5.802	8.036	9.697
<i>Per cent of humus</i>				
Ether-soluble portion.....	2.05	3.13	4.77	1.60
Alcohol-soluble portion.....	1.09	0.76	2.86	2.00
Cold- and hot-water-soluble portions.....	2.58	2.52	3.50	2.60
Hemicelluloses.....	7.15	5.50	1.14	0
Cellulose.....	4.82	4.77	3.20	0
Lignin.....	39.95	34.15	34.76	32.26
Protein.....	32.70	36.26	50.22	60.61
Total accounted for.....	90.34	87.09	100.45	99.07

foregoing; the cellulose and hemicelluloses are either absent entirely or present only in low concentrations, while the nitrogen content is high. Although the relative protein concentration is greater than in the other soil types, it does not comprise most of the humus, as assumed by Remezov. Lignin is not lacking but is actually found in appreciable amounts. The higher protein content in this soil type is no justification for the assumption, which was not based upon experimental evidence, that the humus in serozems consists entirely of microbial cell substance. The possibility is not excluded that some of the nitrogen in these soils may be present, partly at least, in the form of other, non-protein compounds. The average C:N ratio of the two serozems analyzed here is 6.2, whereas the average C:N ratio for the Central Asiatic soils studied by Remezov was 4.5; this suggests the possibility that the humus

in the two American soils is not exactly the same as that of the Asiatic soils. The still narrower C:N ratio in the latter points to a considerable increase in protein content. The difference may here, as well, be due to a natural variation in soil types rather than to a marked change in the nature of the humus.

The rapid decomposition of the organic matter in serozem soils upon cultivation was brought out by Geltzer et al. (5), who found that in some cases as much as 53 per cent of the humus was destroyed upon cultivation for a period of 3 years. It is interesting to note that the loss of nitrogen was less than that of total humus, with the result that the C:N ratio became narrower, changing from 8.2:1 in the original soil to 6.2:1 in the cultivated soil. The humus content of the soil reached an equilibrium, the loss becoming smaller on continued cultivation; the equilibrium was at the lowest point when mineral fertilizers were used, indicating greater decomposition of the humus.

Attention has already been called to the fact that the findings of Geltzer, which are contrary to the results obtained by Remezov and those reported in this paper, of large quantities of hemicelluloses and cellulose in serozem soils were due to an insufficient consideration of the method of determination of these two groups of complexes in the humus. Geltzer determined the carbon in the portion of humus hydrolyzed by dilute mineral acid and calculated it as hemicellulose. This carbon is derived from carbohydrates only to a limited extent in the case of mineral soils; it is formed largely as a result of hydrolysis of some of the soil proteins and other compounds; it is also due partly to the destruction of some of the lignin on prolonged boiling with acid.

#### SUMMARY

Different soil types contain forms of humus which differ considerably in chemical composition.

Humus in podzols is characterized by a high cellulose, a high hemicellulose, and a low protein content. Because of a lack of bases in these soils, the two major constituents of the humus, namely, the lignin and protein, are readily dispersed in the water and are carried down to the lower horizons, where they are precipitated, in the presence of greater base concentration. One need not assume the existence of "humic acids" and "crenic acids," in order to explain the movement of specific organic complexes in the process of podzolization. This process can be much better understood when consideration is given to the mobility of the specific chemical constituents of humus under different soil and environmental conditions.

The humus of the tchernozems is characterized by a narrower carbon-nitrogen ratio, which is nearly 10:1, by a high content of lignin and protein, and by a lower cellulose and hemicellulose concentration. The humus in these soils is fixed because of the abundance of bases, namely, calcium and magnesium.

The humus in chestnut soils approaches in its chemical composition that of the tchernozems; it stands midway between these and the serozems. In

view of the fact, however, that only one soil belonging to this type was analyzed here, no broad conclusions can be drawn.

The humus of the serozems is characterized by a narrow carbon-nitrogen ratio of about 6:1. This is due to the relatively high protein content of this type of humus. Cellulose is completely absent. Hemicelluloses are either absent or present in very low concentrations. Lignins are present, but in somewhat lower amounts than in tchernozems.

As one proceeds from the podzols to the serozems, one finds the following gradual changes in the chemical composition of the humus: 1. A rapid disappearance of the cellulose and hemicelluloses, due to more active decomposition processes. 2. A rapid increase in the nitrogen content of the humus, because of the synthesizing activities of the microorganisms, accompanying the reduction of the carbohydrates. 3. The narrowing of the C:N ratio, based upon the preceding two phenomena. 4. A gradual reduction in lignin content, due to its greater decomposition.

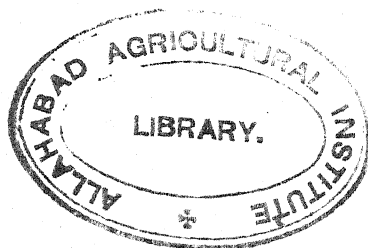
Considerable variation was found among soils belonging to the same general type. Care must, therefore, be exercised in basing definite conclusions upon a large number of soils belonging to each soil type.

#### REFERENCES

- (1) ALEXANDER, L. T., AND BYERS, H. G. 1932 A critical laboratory review of methods of determining organic matter and carbonates in soil. *U. S. Dept. Agr. Tech. Bul.* 317: 1-25.
- (2) BEMMELEN, J. W. VAN 1890 Die Zusammensetzung des Meeresschlicks in den neuen Alluvien des Zuiderzee (Niederlands). *Landw. Vers. Sta.* 37: 239-256.
- (3) BLAIR, A. W., AND PRINCE, A. L. 1928-32 The influence of heavy applications of dry organic matter on crop yields and on the nitrate content of the soil. *Soil Sci.* 25: 281-286; 35: 209-218.
- (4) BOUYOUCOS, G. J. 1932-33 A method for determining combined water and organic matter in soils. *Soil Sci.* 34: 259-267; 36: 471-48.
- (5) GELTZER, F. U., RUBINTSHIK, U. A., AND LASUKOVA, T. P. 1933 On the forms of organic matter in the soil. *Chemiz. Socialist. Agr.* 5: 37-43.
- (6) LIPMAN, J. G., BLAIR, A. W., AND PRINCE, A. L. 1928 Field experiments on the availability of nitrogenous fertilizers, 1923-1927. *Soil Sci.* 26: 1-24.
- (7) LUNT, H. A. 1931 The carbon-organic matter factor in forest soil humus. *Soil Sci.* 32: 27-33.
- (8) RATHER, J. B. 1917 An accurate loss-on-ignition method for determination of organic matter in soils. *Ark. Agr. Exp. Sta. Bul.* 140.
- (9) REMEZOV, N. P. 1932 Contradictory processes as a basis for the genetic soil classification. *Pedology* 27: 178-211.
- (10) REMEZOV, N. P. 1933-34 On the qualitative composition of the organic matter in the soils of U. S. S. R. *Pedology* 28: 383-394; *Ztschr. Pflanzenernähr. Düngung. u. Bodenk.* 30: 285-298, 299-311; 36: 37-52.
- (11) ROBINSON, W. O. 1927 The determination of organic matter in soils by means of hydrogen peroxide. *Jour. Agr. Res.* 34: 339-356.
- (12) SCHOLLENBERGER, C. J. 1927 A rapid approximate method for determining soil organic matter. *Soil Sci.* 24: 65-68.
- (13) SHOREY, E. C. 1930 Some methods for detecting differences in soil organic matter. *U. S. Dept. Agr. Tech. Bul.* 211.



- (14) SPRINGER, U. 1928 Die Bestimmung der organischen, insbesondere der humifizierten Substanz in Böden. *Ztschr. Pflanzenernähr. Düngung. u. Bodenk.* (A) 11: 313-359.
- (15) TIURIN, I. V. 1931 A new modification of the volumetric method of determining soil organic matter by means of chromic acid. *Pedology* 26: 36-47.
- (16) WAKSMAN, S. A. 1929 Chemical nature of soil organic matter, methods of analysis, and the rôle of microorganisms in its formation and decomposition. *Trans. Second Conn. Internatl. Soc. Soil Sci.* (Budapest) Pt. A: 172-197.
- (17) WAKSMAN, S. A. 1933 The origin and nature of humus. *Trans. Second Conn. Internatl. Soc. Soil Sci.* (Denmark) A: 119-132.
- (18) WAKSMAN, S. A., AND DIEHM, R. A. 1929 Chemical and microbiological principles underlying the transformation of organic matter in stable manure in the soil. *Jour. Amer. Soc. Agron.* 21: 795-809.
- (19) WAKSMAN, S. A., AND GERRETSEN, F. C. 1931 Influence of temperature and moisture upon the nature and extent of decomposition of plant residues by microorganisms. *Ecology* 12: 33-60.
- (20) WAKSMAN, S. A., AND REUSZER, H. W. 1930 Ueber die chemische Natur und den Ursprung des Humus im Erdboden. *Cellulosechem.* 11: (10/11).
- (21) WAKSMAN, S. A., AND STEVENS, K. R. 1928 Contribution to the chemical composition of peat: I. Chemical nature of organic complexes in peat and methods of analysis. *Soil Sci.* 26: 113-137, 239-251.
- (22) WAKSMAN, S. A., AND STEVENS, K. R. 1930 A critical study of the methods for determining the nature and abundance of soil organic matter. *Soil. Sci.* 30: 97-116.
- (23) WAKSMAN, S. A., TENNEY, F. G., AND STEVENS, K. R. 1928 The rôle of microorganisms in the transformation of organic matter in forest soils. *Ecology* 9: 126-144.
- (24) WEIS, FR. 1929 Physical and chemical investigations of Danish heath soils (podsoles). K. Danske Vidensk. Selsk., Biol. Meddel. VII, 9.
- (25) WEIS, FR. 1932 Further investigations on Danish heath soils and other podsoles. K. Danske Vidensk. Selsk., Biol. Meddel. X, 3.
- (26) WOLFF, E. 1864 Entwurf zur Bodenanalyse. *Ztschr. Analyt. Chem.* 3: 83-115; also *Landw. Vers. Sta.* 6: 141-171.





## THE AVAILABILITY OF SOIL POTASSIUM<sup>1</sup>

JOHN LAMB, JR.<sup>2</sup>

*Cornell University*

Received for publication January 4, 1935

The potassium content of most mineral soils is relatively high. This fact has led to the widespread belief that with proper methods of soil management the plant would be able to obtain all the potassium necessary for its best development. The method usually suggested involves an increase in the activity of the soil solvents by the use of organic matter in the form of green manure, crop residues, or farm manure.

Early results from the outlying soil experiment fields of Illinois, on gray soils low in general productivity, showed little need for potassium fertilization. After some 12 years of intensive legume cropping, accompanied by the liberal use of limestone considered necessary to grow the legumes, a marked response to potassium fertilization was observed. Twenty-five years' experimental results at the New York State College of Agriculture indicated that the addition of potassium to the soil increased crop yields, although the results for the first few years showed no increase. In these experiments it appears that the natural forces operating were not sufficient to provide adequate available potassium over a period of years, despite the fact that the soil was furnished with liberal amounts of lime and organic matter.

Many attempts have been made to correlate the water-soluble and exchangeable potassium of the soil with the availability of potassium to plants. Von Nostitz (28), Breazeale (7), and Magistad (24) believe that the plant's chief source of potassium is the water-soluble or exchangeable form. The last named investigator as well as Martin (25) also believes that the plant obtains part of its potassium from the non-replaceable form. Gedroiz (14), in his experiments, concluded that plants were able to obtain all the potassium necessary from the non-exchangeable form. Bartholomew and Janseen (3) found it possible to vary the amount of exchangeable potassium through a wide range by means of potassium fertilization. Schollenberger and Dreibebis (30) and Crowther and Basu (12) found that exchangeable potassium was increased by potassium fertilization.

Some attention has been given the ratio of exchangeable calcium to exchangeable potassium. The assimilation of potassium is believed by von

<sup>1</sup> Thesis submitted in partial fulfillment of the requirement for the degree of doctor of philosophy at Cornell University.

<sup>2</sup> Soil Erosion Service, U. S. Department of Agriculture, Ithaca, N. Y.

Nostitz (28) to be definitely related to the amount of lime and magnesia. The importance of this ratio has been mentioned by Barbier (2). Ehrenberg (13) pointed out the harmful influence to plant growth of increasing the supply of lime to a soil low in available potassium.

It has been suggested that the rate of solubility of soil potassium would offer an explanation of the difference between soils in their ability to provide the plant with this element. Bouyoucos (5) found soils differed in their rate of solubility, as measured by the depression of the freezing point, but concluded there was no close relation of this property to soil productivity. No determinations were made of individual solutes. Burd and Martin (9) found that the concentration of electrolytes in the displaced soil solution was higher in the spring than in the fall. This indicated to them that some soils may be unable to maintain during the whole season a concentration of nutrients sufficient to produce normal growth.

It is evident that the manner in which the soil provides the plant with available potassium is not well understood. The purpose of the following investigation is to contribute additional information to the subject.

#### METHODS OF ANALYSIS

Exchangeable potassium and calcium were extracted with normal ammonium acetate adjusted to a pH of 7.07 as suggested by Schollenberger and Dreibebis (31). Such a solution has no significant secondary solubility effect, and a preliminary treatment with a strong alkali is unnecessary in order to replace all exchangeable hydrogen. One hundred cubic centimeters of the ammonium acetate solution was added to 10 gm. of air-dry soil in a 250-cc. Erlenmeyer flask, and the mixture was shaken for 10 minutes. The contents of the flask were transferred to a dry filter and washed twice with two 50-cc. portions of the ammonium acetate solution.

The determination of potassium in this extract was made by the sodium cobaltic nitrite method as used and described by Snider.<sup>3</sup> The solution of sodium cobaltinitrite was prepared by adding 25 gm. of the reagent to 100 cc. of water. The mixture was kept on ice one to two hours in the dark, filtered through asbestos, and held at 10°C. or below in the dark until needed. The solution obtained by extracting the soil with normal ammonium acetate was placed in 250-cc. beakers and evaporated to dryness on the steam bath. Five cubic centimeters of 5 to 10 per cent  $H_2O_2$  was added to the residue, and the resulting solution was evaporated to dryness. The process was repeated three times. The residue was taken up with about 10 cc. of hot water, and 20 per cent NaOH was added until the solution was alkaline to phenolphthalein. The solution was boiled 3 to 10 minutes to expel traces of ammonia, the sides of the beaker were washed down with hot water during the process, and the boiling was continued until a volume of about 5 cc. was attained. The solu-

<sup>3</sup> The author is indebted to H. J. Snider of the Illinois Experiment Station for a description of the method followed.

tion was then filtered through a No. 00 9-cm. Swedish filter paper. The beaker and filter were washed with small amounts of hot water until the filtrate and washings, received in 250-cc. Pyrex beakers, reached a volume of about 25 cc. Beginning with the filtering process care was taken to exclude fumes of ammonia from the laboratory as was emphasized by Milne (26). The filtrate was made acid with 1-1 acetic acid, and then 5 drops more of the acid was added. Ten cubic centimeters of redistilled, 95 per cent, ethyl alcohol was added, and the beakers were placed on ice or otherwise reduced to a temperature of 10°C. or below. Five cubic centimeters of a 25 per cent solution of sodium cobaltic nitrite was then added, and the beakers were held at 10°C. or below in the dark for one to twenty-four hours. This solution, containing the precipitate of potassium cobaltinitrite, was filtered through the asbestos pad of a Gooch crucible which had just been washed with ice water. The precipitate was washed with 4-cc. portions of ice water until free of alcohol. Gentle suction was used. The crucible was placed pad intact into the original beaker, about 200 cc. of boiling water and 6 cc. of 6 *N* H<sub>2</sub>SO<sub>4</sub> were added, and the mixture was titrated at once with about 0.05 *N* KMnO<sub>4</sub> to a faint permanent pink. The asbestos may be used repeatedly. One cubic centimeter of 0.05 *N* KMnO<sub>4</sub> is equivalent to 0.0003259 gm. of K.

The reagents used in the determinations were carefully prepared. The alcohol was redistilled. The asbestos was prepared according to the method described by Morrow (27) for sugar analysis. The potassium permanganate solution was stored in the dark and checked against sodium oxalate at frequent intervals. A blank determination of reagents was made for each series of determinations.

The cobaltic nitrite method has certain advantages over the ordinary platinic chloride procedure especially where small quantities of potassium are to be determined. However, since the method is open to criticism if not carefully controlled it was thought desirable to examine certain details of the procedure and to determine its reliability with the platinic chloride method.

A solution of K<sub>2</sub>SO<sub>4</sub> was made up containing 0.5 mgm. of potassium per cubic centimeter. This concentration was checked by the platinic chloride method. Table 1 shows the influence of the time of standing after addition of the solution of cobaltinitrite to a solution containing 2 mgm. of potassium as K<sub>2</sub>SO<sub>4</sub>. The results indicate that a period of one hour is ample to precipitate the potassium from the solution.

Table 2 shows determination of potassium by the cobaltic nitrite method in a solution containing 0.5 mgm. per cubic centimeter.

In the case of 10-gm. soil samples 0.25 mgm. of potassium represents 25 p.p.m. It was found possible to check duplicate determinations of exchangeable potassium within 3 p.p.m. by means of the sodium cobaltic nitrite method.

The determination of total potassium in soils was made by fusing 1 gm. of soil with 5 gm. of Na<sub>2</sub>CO<sub>3</sub>; the flux was taken up with hot water and evaporated to dryness; and the silica was eliminated in the usual manner. The

filtrate from the precipitate of silica was made up to 250-cc. volume, and the potassium of a 25-cc. aliquot was determined by the cobaltic nitrite method.

To check the accuracy of this method the potassium was determined in the original samples of two New York soils, the total potassium of which had been

TABLE 1

*Effects of time of standing on precipitation of potassium from  $K_2SO_4$  solution to which has been added cobaltic nitrite solution*

$K_2SO_4$  solution originally contained 2 mgm. K

TIME OF STANDING	K RECORDED	TIME OF STANDING	K RECORDED
hours	mgm.	hours	mgm.
$\frac{1}{4}$	1.92	2	2.10
$\frac{1}{2}$	1.98	21	2.08
$\frac{3}{4}$	1.94	51	2.23
1	2.02	78	2.02

TABLE 2

*Potassium determination by cobaltic nitrite method*

SOLUTION	K PRESENT	K FOUND	K RECOVERED
cc.	mgm.	mgm.	per cent
0.5	0.25	0.29	116
1.0	0.50	0.46	92
2.0	1.00	1.08	108
3.0	1.50	1.44	96
4.0	2.00	2.00	100
5.0	2.50	2.50	100
6.0	3.00	2.82	94
7.0	3.50	3.29	94

TABLE 3

*Comparison of cobaltic nitrite and platinic methods of determining total potassium of New York soils*

SOILS	POTASSIUM FOUND BY	
	Platinic chloride method	Cobaltic nitrite method
	per cent	per cent
21A	2.19	2.20
70A	1.56	1.54

determined by the platinic chloride method and reported by Bizzell (5). These soils were reported as 21A, a Volusia silt loam from Allegany County, and 70A, a Duchess silt loam from Duchess County.

Table 3 shows a comparison of cobaltic nitrite and platinic methods of determining the total potassium of two New York soils.

All determinations as reported were made in duplicate. In order to avoid any possibility of a systematic error the duplicate determinations in each case were made at different periods.

Exchangeable calcium was determined by precipitation as  $\text{CaC}_2\text{O}_4$  and titration of the same with 0.1 *N*  $\text{KMnO}_4$ .

Nitrate nitrogen was determined colorimetrically in an extract obtained from one part of soil and five parts of water.

Base exchange capacity was determined by ammonia absorption. The soil was leached with ammonium acetate according to the method of Chapman and Kelley (10). The ammonium fixed by the soil was determined by digestion with an excess of  $\text{MgO}$  and distillation into 0.1 *N*  $\text{H}_2\text{SO}_4$ .

The hydrogen-ion concentration was determined by means of the quinhydrone electrode. Electrical resistance of solutions was determined by means of a modification of the wheatstone bridge, as designed by Briggs (8).

#### *Relation of Crop Yields and Fertilization to Exchangeable Potassium*

A history of the soils used is necessary before the results of the chemical studies are considered. The Ewing soil experiment field, located in southern Illinois, was established in 1910. The soil is a mature, imperfectly drained, gray silt loam, with a slowly pervious tight clay layer 18 to 20 inches below the surface. The slope is 3 per cent or less. The rotation was wheat (sweet clover seeding), corn, oats, and sweet clover seed crop, as described by Bauer, Smith, and Smith (4). The soil treatments were as follows:

R—residues, corn stalks, sweet clover catch crop. Straw was included previous to 1922

L—limestone, 9 tons applied during the period 1910–1922.

P—rock phosphate, 4 tons applied during the period 1910–1924.

K—Kainit, 400 pounds, applied before corn, and 400 pounds before wheat in the rotation.

M—barnyard manure. To the “M” alone plot 3.2 tons per the rotation ending 1930, and to the “ML” plot 8.9 tons per the same period, were applied before corn in each case. These amounts were equivalent to the dry weight of the crops removed from the respective plots.

After the use of limestone and sweet clover for about 12 years, the crops—especially corn—appeared to suffer from lack of potassium. The yields of corn for two periods are shown in table 4. This condition, although more serious at Ewing, was found under like circumstances on similar soils in other locations in the state.

In 1927 straw at the rate of 3 tons per acre was spread over the soil just after corn planting, left on the ground for 5 weeks, and then removed. Frequent rains occurred during the period. The yields for the RL and RLP plots indicate that available potassium was furnished by the straw. A decrease in available nitrogen, due to the increase in activity of the soil organisms, may also have been beneficial to the crop.

Soil samples representing the soil layers  $A_1$ ,  $A_3$ , and  $B_1$  were collected from the experiment field, June 1930.

The RL and RLP plots (table 5) show an average of 23 and 25 p.p.m. of exchangeable potassium in comparison with 31 p.p.m. for the untreated plot. Ames and Simon (1) as well as Crowther and Basu (12) obtained similar

TABLE 4  
*Ewing soil experiment field yields of corn with soil treatments indicated*

SOIL TREATMENT	AVERAGE ACRE YIELD 1915-16	ACRE YIELD 1927	ADDITIONAL TREATMENT 1927	ACRE YIELD 1927
	<i>bu.</i>	<i>bu.</i>		<i>bu.</i>
O	21	2	Straw	7
R	17	1	Straw	7
RL	49	5	Straw	22
RLP	47	5	Straw	26
RLPK	60	52	Straw	50
ML	59	53	Straw	40

TABLE 5  
*Exchangeable potassium and pH of Ewing soil*

SERIES	SOIL LAYERS	SOIL TREATMENT AND PLOT NUMBER													
		2 M		3 ML		6 R		7 RL		8 RLP		9 RLPK		None	
		K	pH	K	pH	K	pH	K	pH	K	pH	K	pH	K	pH
		<i>p.p.m.</i>		<i>p.p.m.</i>		<i>p.p.m.</i>		<i>p.p.m.</i>		<i>p.p.m.</i>		<i>p.p.m.</i>		<i>p.p.m.</i>	
100	A <sub>1</sub>	41	4.7	38	7.6	31	4.3	23	7.7	14	7.7	58	7.7	23	4.6
100	A <sub>3</sub>									21	5.1	28	5.3	28	4.7
100	B <sub>1</sub>									115	5.2	132	5.2	122	5.4
200	A <sub>1</sub>	38	4.8	28	6.8	35	4.8	20	7.2	31	7.3	40	6.8	28	4.9
200	A <sub>3</sub>									25	5.0	33	5.2	33	4.9
200	B <sub>1</sub>									126	5.0	142	4.7	144	5.1
300	A <sub>1</sub>	39	4.4	50	6.7	40	4.4	23	6.5	27	6.8	40	6.6	39	4.6
300	A <sub>3</sub>									28	5.2	30	5.0	88	4.8
300	B <sub>1</sub>									104	5.2	104	5.0	165	5.3
400	A <sub>1</sub>	50	4.5	52	6.7	47	4.5	26	6.4	30	6.2	92	6.3	36	4.5
400	A <sub>3</sub>									48	5.4	47	5.5	47	4.9
400	B <sub>1</sub>									125	4.8	136	5.0	119	5.1
Av.	A <sub>1</sub>	42		42		38		23		25		56		31	
Av.	A <sub>3</sub>									30		34		49	
Av.	B <sub>1</sub>									117		128		137	

results. The experiments of Bartholomew and Janseen (3) indicated that plants could reduce the exchangeable potassium below 25 p.p.m. only with difficulty.

Potassium fertilization doubled the exchangeable potassium, as shown in



table 6, but this rapidly falls to the lower level apparently as a result of removal by crops. The manure (table 7) maintains a level little higher than that of the untreated plots, but furnished a supply adequate for large crop yields.

TABLE 6  
*Effect of kainit on the exchangeable potassium of the Ewing soil*  
Soil samples collected June 1930

400 LBS. KAINIT APPLIED FOR		PLOT	K FOUND
Crop of	Crop of		
1927	1930	109	<i>p.p.m.</i> 58
1927	1928	209	40
1928	1929	309	40
1929	1930	409	92

TABLE 7  
*Effect of manure on the exchangeable potassium of the Ewing soil*  
Soil samples collected June 1930

CROP OF	3.2 TONS MANURE PER ACRE		8.9 TONS MANURE PER ACRE	
	Plot	K found	Plot	K found
		<i>p.p.m.</i> 400 lb		<i>p.p.m.</i>
1927	102	41	103	38
1928	202	38	203	28
1929	302	39	303	50
1930	402	50	304	52

TABLE 8  
*Total and exchangeable potassium, Ewing soil*  
Expressed in pounds per acre

PLOT	SOIL LAYER	EXCHANGEABLE K	TOTAL K
108	A <sub>1</sub>	14	12,500
	A <sub>2</sub>	21	13,700
	B <sub>1</sub>	115	14,300
109	A <sub>1</sub>	58	12,500
	A <sub>2</sub>	28	13,400
	B <sub>1</sub>	132	13,700

The high amount of exchangeable potassium of the B<sub>1</sub> soil layer (table 8) compared with that of the upper layers, suggests that potassium carried in solution from the surface soil was fixed to some extent in the B<sub>1</sub> by replacing other cations of the soil complex. Or that the replaceable potassium of this

layer was not changed through leaching or soil management to the extent of that of the surface layer. The former theory has been suggested by Lyon, Bizzell, Wilson, and Leland (21), and by MacIntire (22). It would seem probable that this region of higher concentration would offer a supply of readily available potassium to deep-rooted legumes. The growth of sweet clover and succeeding crops, on plots receiving no potassium fertilization, on the Ewing field does not agree with this theory.

#### THE RELATION OF TOTAL TO EXCHANGEABLE POTASSIUM

There is little relation between the total potassium and the exchangeable potassium; plot 109 A<sub>1</sub> layer (table 8) has over four times as much of the latter form as the same layer plot 108, yet both have the same amount of total potassium. The B<sub>1</sub> layer plot 108 has less exchangeable potassium, and more of the total, than the same layer plot 109.

#### RELATION OF EXCHANGEABLE CALCIUM TO EXCHANGEABLE POTASSIUM

The relations of exchangeable calcium to exchangeable potassium are brought out in table 9. Fertilization increased the exchangeable calcium in the surface layer and in the A<sub>3</sub> layer, but it affected the potassium of the surface layer only.

In many instances the heavy application of limestone lowered the hydrogen-ion concentration below the neutral point and retarded the rate of change from the complex to simple forms of soil potassium. The work of Lyon, Bizzell, Wilson, and Leland (21), Magestad (24), MacIntire (22), and others bears out this idea. It was found by analysis that the limed soils of the Ewing field contained no calcium as calcium carbonate. Tables 9 and 10 reveal that the adsorptive complexes of the limed soils were practically saturated with calcium in the A<sub>1</sub> layer. MacIntire and Sanders (23) suggested that such freshly formed calcium and magnesium absorption complexes were more readily hydrolyzable than freshly formed potassium absorption complexes.

The ratio of calcium to potassium in the untreated soil was 28; in the RLPK plot, 59; and in the RLP plot, 180. Such a wide ratio as the last might lead to serious nutritional disturbances of the plant. Von Nostitz (28) believes that a certain ratio of calcium to potassium is best for normal growth. Ehrenberg (13), Lagatu and Maume (18), and Lipman, Blair, and Prince (19) have pointed directly to a decreased absorption of potassium by plants due to liming. Volk and Truog (34) believe that calcium antagonism to potash absorption may explain some of the pronounced responses to potash fertilization obtained on neutral and calcareous soils high in nitrates and hence in soluble calcium salts.

A relatively high concentration of calcium in the soil solution may retard the entrance of potassium into the plant. True (33) believes that the presence of a certain amount of available calcium in the cultural solution is necessary to maintain normal permeability relations of the cells of absorbing roots of

TABLE 9

*Effect of cropping and fertilization on exchangeable potassium and calcium*

Milligram equivalents of exchangeable calcium and potassium, the base exchange capacity, and the pH of Ewing soil.

PLOT	SOIL LAYER	TREATMENT	CALCIUM	POTASSIUM	AMMONIA ABSORBED	pH
			<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	
108	A <sub>1</sub>	RLP	9.2	0.036	9.0	7.7
	A <sub>3</sub>	RLP	3.6	0.054	8.5	5.1
	B <sub>1</sub>	RLP	3.4	0.294	19.5	5.2
109	A <sub>3</sub>	RLPK	9.0	0.148	9.7	7.7
	A <sub>3</sub>	RLPK	4.2	0.072	8.7	5.3
	B <sub>1</sub>	RLPK	4.5	0.341	21.0	5.2
110	A <sub>1</sub>	O	1.4	0.059	8.2	4.6
	A <sub>3</sub>	O	1.5	0.072	9.0	4.7
	B <sub>1</sub>	O	3.9	0.313	20.5	5.4
208	A <sub>1</sub>	RLP	8.8	0.079	8.5	7.3
	A <sub>3</sub>	RLP	3.5	0.064	6.4	5.0
	B <sub>1</sub>	RLP	3.6	0.323	20.0	5.0
209	A <sub>1</sub>	RLPK	7.7	0.104	9.0	6.8
	A <sub>3</sub>	RLPK	3.7	0.084	7.5	5.2
	B <sub>1</sub>	RLPK	4.3	0.363	20.0	4.7
210	A <sub>1</sub>	O	1.8	0.072	7.9	4.9
	A <sub>3</sub>	O	2.5	0.084	9.2	4.9
	B <sub>1</sub>	O	4.4	0.369	23.4	5.1
308	A <sub>1</sub>	RLP	9.1	0.069	8.6	6.8
	A <sub>3</sub>	RLP	3.7	0.072	7.8	5.2
	B <sub>1</sub>	RLP	3.4	0.266	13.3	5.2
309	A <sub>1</sub>	RLPK	7.8	0.104	9.5	6.6
	A <sub>3</sub>	RLPK	3.6	0.077	8.1	5.0
	B <sub>1</sub>	RLPK	4.3	0.266	17.0	5.0
310	A <sub>1</sub>	O	3.0	0.100	9.1	4.6
	A <sub>3</sub>	O	2.4	0.215	10.5	4.8
	B <sub>1</sub>	O	5.6	0.422	22.5	5.3
408	A <sub>1</sub>	RLP	9.0	0.074	10.6	6.2
	A <sub>3</sub>	RLP	6.2	0.126	10.1	5.4
	B <sub>1</sub>	RLP	5.0	0.320	18.9	4.8
409	A <sub>1</sub>	RLPK	8.8	0.236	10.5	6.3
	A <sub>3</sub>	RLPK	5.5	0.120	9.9	5.5
	B <sub>1</sub>	RLPK	5.6	0.348	20.3	5.0
410	A <sub>1</sub>	O	3.2	0.092	9.9	4.5
	A <sub>3</sub>	O	3.1	0.120	10.2	4.9
	B <sub>1</sub>	O	4.1	0.300	18.9	5.1

TABLE 10

*The ratio of milligram equivalents of exchangeable calcium to exchangeable potassium, of calcium to base exchange capacity, and of potassium to Ewing soil*

PLOT	SOIL LAYER	TREATMENT	RATIO CALCIUM TO POT	RATIO CALCIUM TO ABSORBED AMMONIA	RATIO POTASSIUM TO ABSORBED AMMONIA
108	A <sub>1</sub>	RLP	256	1.02	0.004
	A <sub>3</sub>	RLP	67	0.24	0.006
	B <sub>1</sub>	RLP	11	0.18	0.015
109	A <sub>1</sub>	RLPK	61	0.93	0.015
	A <sub>3</sub>	RLPK	60	0.48	0.008
	B <sub>1</sub>	RLPK	13	0.21	0.016
110	A <sub>1</sub>	O	24	0.17	0.007
	A <sub>3</sub>	O	21	0.17	0.008
	B <sub>1</sub>	O	13	0.19	0.015
208	A <sub>1</sub>	RLP	111	1.04	0.009
	A <sub>3</sub>	RLP	55	0.55	0.010
	B <sub>1</sub>	RLP	11	0.18	0.016
209	A <sub>1</sub>	RLPK	74	0.86	0.010
	A <sub>3</sub>	RLPK	44	0.49	0.011
	B <sub>1</sub>	RLPK	12	0.22	0.018
210	A <sub>1</sub>	O	25	0.20	0.009
	A <sub>3</sub>	O	30	0.27	0.009
	B <sub>1</sub>	O	12	0.19	0.016
308	A <sub>1</sub>	RLP	232	1.06	0.008
	A <sub>3</sub>	RLP	51	0.47	0.009
	B <sub>1</sub>	RLP	13	0.26	0.020
309	A <sub>1</sub>	RLPK	75	0.82	0.011
	A <sub>3</sub>	RLPK	47	0.44	0.010
	B <sub>1</sub>	RLPK	16	0.25	0.016
310	A <sub>1</sub>	O	30	0.33	0.010
	A <sub>3</sub>	O	11	0.23	0.022
	B <sub>1</sub>	O	13	0.25	0.042
408	A <sub>1</sub>	RLP	122	0.85	0.007
	A <sub>3</sub>	RLP	24	0.62	0.013
	B <sub>1</sub>	RLP	16	0.27	0.017
409	A <sub>1</sub>	RLPK	37	0.84	0.023
	A <sub>3</sub>	RLPK	46	0.55	0.012
	B <sub>1</sub>	RLPK	16	0.28	0.017
410	A <sub>1</sub>	O	35	0.32	0.009
	A <sub>3</sub>	O	26	0.30	0.012
	B <sub>1</sub>	O	14	0.22	0.016

higher green plants. Eckerson working with True (33), using young corn plants, substituted the calcium of the culture solution with potassium. An increase in permeability occurred, and the content of the root cells moved outward with fatal results to the plants. It is reasonable to believe that this reaction would be reversible to some extent, and in a solution containing an excess of calcium the effect on permeability may be such as to retard the entrance of essential ions.

The poor growth of corn on the Ewing field occurred on those plots where the conditions favored a high concentration of calcium in the soil solution: a soil high in nitrates with an adsorptive complex saturated with calcium. Whiting and Richmond (35) working with soils similar to that of the Ewing field found that plowing in a crop of sweet clover for corn often supplied 150 pounds of nitrogen per acre. This would be equivalent to over 650 pounds of nitric acid in its action on the soil bases. Sears (32) found a reduction of nitrate content as well as an addition of potassium salts beneficial on certain alkali soils of northern Illinois.

In cases where lime causes a decrease in growth the effect may be due to the decrease in permeability caused by the calcium with a consequent decrease in intake of the essential elements. The addition of any cation which would increase permeability should prevent the injurious effect of calcium. Kainit, a mixed salt, has been very effective in relieving potassium deficiency on the Ewing field, possibly for this reason. Gerlach (15) and many others have presented evidence to show that sodium partially replaces potassium where the latter is present in small amounts.

#### RATE OF SOLUBILITY OF SOIL POTASSIUM

It has been suggested that the rate of solubility of soil potassium is a better index of availability than is the amount soluble at a given time. The Ewing soil already described and four New York State soils were selected for study. The New York soils were as follows: an Ontario loam from Monroe County and a Volusia silt loam from Turkey Hill, Tompkins County. The first two of these soils responded to potassium fertilization; the last two did not, as reported by Lyon (20).

The soils were leached with distilled water until the electrical resistance of the leachate approached the resistance of distilled water. At this point it was assumed that the materials capable of carrying an electric current, which would include the highly ionized potassium compounds, had been carried out of the soil. The soils were air dried and held at room temperature and optimum moisture for 30 days and again leached. Following this it was again air dried and held under the same conditions for 180 days and leached a third time.

The first and second leachings were collected in successive portions representing 100 cc. of leachate per 50 gm. of soil. The potassium was determined in each portion. The third leaching process was so slow as a result of the

puddled condition of the soil that no attempt was made to divide it into separate portions. The results are shown in table 11.

All the soils were rapidly reduced to the point where about the same amount of potassium was found in successive portions of the leachate. There seemed to be little substantial increase in this amount during the period of incubation. Barbier (4) found that in extracting a soil by percolation with water the first portions of the percolate contained practically all the water-soluble potassium.

TABLE 11

*Potassium extracted by successive portions of distilled water, 100 cc. per 50 gm. of soil, and electrical resistance of extract*

100-cc. PORTIONS DISTILLED WATER	ONTARIO		DUTCHESS		VOLUSIA ALLEGHENY		VOLUSIA TURKEY HILL	
	K	Resist- ance	K	Resist- ance	K	Resist- ance	K	Resist- ance
	<i>p.p.m.</i>	<i>ohms</i>	<i>p.p.m.</i>	<i>ohms</i>	<i>p.p.m.</i>	<i>ohms</i>	<i>p.p.m.</i>	<i>ohms</i>
1	4.1	550	14.0	250	15.0	700	28.5	1150
2	3.8	5000	3.2	1600	8.8	2900	12.4	2700
3	3.0	7250	1.6	5000	6.1	5500	8.6	5000
4	3.7	8000	2.9	6500	7.9	8000	13.5	6500
5		9000		8500		9000		8750
6	...	....		9000		....		9000
Total....	14.6		22.7		37.8		63.0	

*Soil incubated 30 days at room temperature and optimum moisture*

1	2.7	3000	2.6	4300	3.1	3300	2.8	4200
2	2.1	5500	2.0	8500	4.2	7000	2.8	6800
3	2.4	6000	1.2	9000	3.4	9000	2.6	9000
4	2.7	9000	2.0	9000	2.8	9000	2.3	9000
5	...	....	2.3	9000	3.1	9000	2.3	9000
Total....	9.9		10.1		16.6		12.6	

*Soil incubated 180 days at room temperature and optimum moisture*

1	...	1500	...	1000	...	2300	...	1200
2	...	2900	...	2800	...	4500	...	2600
3	...	3000	...	5000	...	5500	...	6000
Total....	3.3		4.1		6.2		5.3	

Exchangeable potassium was determined before and after each leaching. The results indicate (table 12) that a part of that recovered in the leachate had been at the expense of the replaceable form. Coles and Morison (11) by alternate washing and drying at 98°C. were able to remove all the exchangeable bases from soils.

The Turkey Hill Volusia, which showed the largest increase for potassium fertilization (20), gave the highest amount of water-soluble potassium. On-

tario loam gave no increase for such fertilization and contained a small amount of water-soluble and exchangeable potassium.

Water-soluble potassium does not represent the entire amount in the soil available to plants, but if the soil were able to maintain the concentrations found, according to Parker and Pierre (29) it would be ample for plant needs. Hoagland and Martin (17) found that the concentration of potassium present in the displaced soil solution before and after growth of a crop could be very low yet effect an adequate supplying power.

TABLE 12

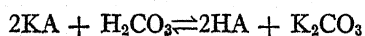
*Potassium leached from soils with distilled water at the intervals and with the soil treatment indicated, and  $\text{NO}_3$  at the time of leaching*

SOIL	NO. 3	K	SOIL TREATMENT*	NO. 3	K	SOIL TREATMENT	NO. 3	K
	p.p.m.	FIRST LEACHING p.p.m.		p.p.m.	LEACHED AT 30 DAYS p.p.m.		p.p.m.	LEACHED AT 210 DAYS p.p.m.
Ontario	230	10.9	None	28	6.2	None	130	3.3
			Sugar N	40	3.9	Sugar NLP	86	4.1
Dutchess	612	18.8	None	49	5.8	None	175	4.1
			Sugar N	33	6.1	Sugar NLP	26	3.9
Volusia A <sub>1</sub>	160	29.9	None	43	10.7	None	49	6.2
			Sugar N	37	6.0	Sugar NLP	432	3.5
Volusia Turkey Hill	23	49.5	None	40	8.2	None	216	5.3
			Sugar N	47	5.1	Sugar NLP	286	2.3
				58	5.7	None	135	3.3
Ewing 110						Sugar NLP	203	1.2
Ewing 110L					2.7	None	154	2.0
Ewing 107				34	4.1	None	115	5.0
						Sugar NLP	124	4.5

\* Soils were maintained at room temperature and optimum moisture during the interval between leachings. After the first leaching, 3,000 p.p.m. dextrose and  $(\text{NH}_4)\text{CO}_3\text{HO}$  equivalent to 150 p.p.m. of  $\text{NO}_3$  were applied. After the second leaching, in the case of the New York soils, and after the first, in the case of Ewing soil, dextrose at the rate of 5,000 p.p.m.,  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$  equivalent to 200 p.p.m. of  $\text{NO}_3$ , 56 p.p.m. of superphosphate, and 2,000 p.p.m. of lime as finely ground  $\text{CaCO}_3$  were applied.

After the first leaching, 3,000 p.p.m. dextrin and  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$  equivalent to 130 p.p.m. of nitrate were added to a part of each soil. After the second leaching, to the same soils were applied dextrin at the rate of 5,000 p.p.m.,  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$  equivalent to 200 p.p.m. of nitrate, 56 p.p.m. of superphosphate, and 2,000 p.p.m. of finely ground limestone. The appearance of nitrate nitrogen was considered an indication that the soil organism had used up the sugar.

We may represent the process of the change from the complex to the simple form of soil potassium, by the following reaction:



in which KA represents the complex form. Factors forcing the reaction to the right are the pressure of  $\text{CO}_2$  and removal of the product  $\text{K}_2\text{CO}_3$ . Theoretically, high activity of the soil organisms should bring about both these conditions. A reduction in their activity would force the reaction toward

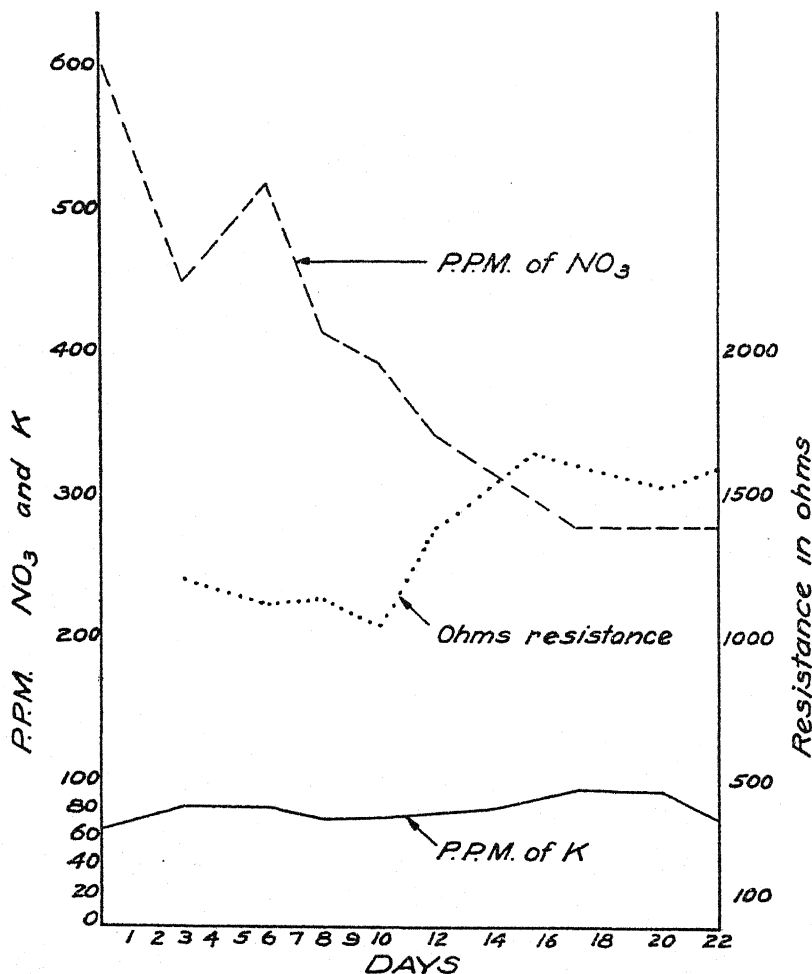


FIG. 1. EFFECT OF THE ADDITION OF 5,000 P.P.M. OF DEXTRIN TO A DUTCHESS SILT LOAM ON THE POTASSIUM EXTRACTED BY  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , ON THE  $\text{NO}_3$  CONTENT, AND ON THE RESISTANCE OFFERED TO AN ELECTRIC CURRENT BY A 5.1 WATER EXTRACT

the left, as a result of a decrease in  $\text{CO}_2$  pressure and the increased amount of the simple form of potassium. Bartholomew and Janseen (5) contend that such a reaction is readily reversible.

The results (table 12) show that at the end of the first incubation period



only one soil receiving dextrose and ammonium carbonate had more water-soluble potassium than the untreated soil. With some of the soils it was thought possible that the activity of the soil organism was still at a relatively high level, and a part of the easily soluble potassium might have been held in their bodies.

The following experiment was carried out in order to determine the influence of an increase in number of the soil organisms upon the exchangeable potassium. Dextrin at the rate of 5,000 p.p.m. was added to a Duchess silt loam, and at frequent intervals determinations were made of total nitrates, exchangeable potassium, and water-soluble materials by the resistance method. The results are shown in figure 1.

The nitrates and total electrolytes showed a steady decrease in concentration; but, after 16 days remained constant. Exchangeable potassium shows a slight increase. It is possible that the demands of the increased numbers of soil organisms were balanced by the solubility effect of the increased CO<sub>2</sub> pressure. Hibbard (16) found that the liberation of much CO<sub>2</sub> is not necessarily followed by a great increase of solubility of soil minerals.

#### SUMMARY

On the Ewing soil high crop yields were maintained only by the addition of potassium.

Potassium fertilization increased the amount of exchangeable potassium until utilized by the crop.

The B<sub>1</sub> soil layer contained much more adsorbed potassium than the A<sub>1</sub> or A<sub>3</sub>.

No relation was found between the total and exchangeable forms of soil potassium.

Fertilization did not affect the exchangeable potassium of the A<sub>3</sub> or B<sub>1</sub> layer or the exchangeable calcium of the B<sub>1</sub> layer.

Potassium starvation in the Ewing soil was associated with low exchangeable potassium and high exchangeable calcium.

The methods used showed no significant difference in the rate at which exchangeable and water-soluble potassium were replenished from the reserve supply of the soils.

There appears to be little relation between response to potassium fertilization and exchangeable or water-soluble potassium for the soils used.

The addition of sugar to a soil high in nitrates reduced the nitrate level, reduced the level of electrolytes, and slightly increased the exchangeable potassium.

#### REFERENCES

- (1) AMES, J. W., AND SIMON, R. H. 1924 Soil potassium as affected by fertilizer treatment and cropping. Ohio Agr. Exp. Sta. Bul. 379.
- (2) BARBIER, G. 1932 Le potassium dans les solutions du sol et l'échange de cations. Ann. Agron. (Nouvelle Ser. 2<sup>e</sup> Année) 5: 628-653.

- (3) BARTHOLOMEW, R. P., AND JANSEEN G. 1931 The rate of absorption of potassium by plants and its possible effect upon the amount of potassium remaining in soils from applications of potassium fertilizers. *Ark. Agr. Exp. Sta. Bul.* 265.
- (4) BAUER, F. C., SMITH, R. S., AND SMITH, L. H. 1926 The Illinois experiment fields. *Ill. Agr. Exp. Sta. Bul.* 273: 41-327.
- (5) BIZZELL, J. A. 1930 The chemical composition of New York soils. Cornell (N. Y.) Agr. Exp. Sta. Bul. 513.
- (6) BOUYOUCOS, G. J. 1919 Rate and extent of solubility of soils under different treatments and conditions. *Mich. Agr. Exp. Sta. Tech. Bul.* 44.
- (7) BREAZEALE, J. F. 1928. Soil zeolites and plant growth. *Ariz. Agr. Exp. Sta. Tech. Bul.* 21.
- (8) BRIGGS, L. J. 1899 Electrical instruments for determining the moisture, temperature, and soluble salt content of soils. U. S. Dept. Agr. Div. Soils. Bul. 15.
- (9) BURD, J. S., AND MARTIN, J. E. 1925 Secular and seasonal changes in the soil solution. *Soil Sci.* 18: 151-167.
- (10) CHAPMAN, H. D., AND KELLEY, W. P. 1930 The determination of the replaceable bases and the base-exchange capacity of soils. *Soil Sci.* 30: 391-406.
- (11) COLES, H. G., AND MORISON, C. G. 1932 Dehydration, soil acidity and exchangeable bases. *Soil Sci.* 33: 115-124.
- (12) CROWTHER, E. M., AND BASU, J. K. 1931 Studies on soil reaction. VIII. The influence of fertilizers and lime on the replaceable bases of a light acid soil after 50 years of continuous cropping with barley and wheat. *Jour. Agr. Sci.* 21: 689-715.
- (13) EHERNBERG, P. 1919 Das Kalk-Kali Gesetz. *Landw. Jahrb.* 54: 1-159.
- (14) GEDROIZ, K. 1931 Exchangeable cations of the soil and the plant: 1. Relation of plant to certain cations fully saturating the soil exchange capacity. *Soil Sci.* 32: 51-63.
- (15) GERLACH, M. 1901-02 The action of kainit and high-percentage potash salts. *Fühl-ing's Landw. Ztg.* 50 (1901) 377-338, 409-416. *Exp. Sta. Rec.* 13: 539.
- (16) HIBBARD, P. L. 1919 Changes in composition of the soil and of the water extract of the soil, following addition of manure. *Soil Sci.* 7: 259-272.
- (17) HOAGLAND, D. R., AND MARTIN, J. C. 1933 Absorption of potassium by plants in relation to replaceable, non-replaceable, and soil solution potassium. *Soil Sci.* 36: 1.
- (18) LAGATU, H., AND MAUME, L. 1928 Antagouime du calcaire, a l'absorption de la potasse par la vigne. *Comm. Cong. Internatl. du Vin et du Pin Maritime*, Bordeaux.
- (19) LIPMAN, J. G., BLAIR, A. W., AND PRINCE, A. L. 1926 Effect of lime and fertilizers on the potash content of soil and crop. *Internal. Rev. Sci. and Pract. Agr.* [Rome] 4: 546-553. (Reprinted in *Proc. Internatl. Soc. Soil Sci.* (N. S.) 2: 201-208.
- (20) LYON, T. L. 1932 Is the soil type homogenous with respect to its fertilizer needs? *Jour. Amer. Soc. Agron.* 24: 58-71.
- (21) LYON, T. L., BIZZELL, J. A., WILSON, B. D. AND LELAND, E. W. 1930 Lysimeter experiments III, records for tanks 3 to 12 during the years 1910-1924 inclusive. Cornell (N. Y.) Agr. Exp. Sta. Mem. 134.
- (22) MACINTIRE, W. H. 1919 The liberation of native soil potassium induced by different calcic and magnesian materials as measured by lysimeter leachings. *Soil Sci.* 8: 337-396.
- (23) MACINTIRE, W. H., AND SANDERS, K. B. 1930 The fixation of the potash of a green manure by liming materials. *Soil Sci.* 29: 109-117.
- (24) MAGISTAD, O. C. 1928 The hydrolysis of sodium and potassium zeolites with particular reference to potassium in the soil solution. *Ariz. Agr. Exp. Sta. Tech. Bul.* 22.

- (25) MARTIN, J. C. 1929 Effect of crop growth on the replaceable bases in some Californian soils. *Soil Sci.* 27: 123-136.
- (26) MILNE, G. 1929 Cobaltinitrite (vol.) method of estimating potassium in soil extracts. *Jour. Agr. Sci.* 19: 541-552.
- (27) MORROW, C. A. 1927 Biochemical Laboratory Methods. John Wiley & Sons, Inc., New York.
- (28) NOSTITZ, A. VON 1922-3 The importance of exchangeable soil potassium for plant nutrition. *Jour. Landw.* 70 (1922): 45-71. *Exp. Sta. Rec.* 48 (1923): 214.
- (29) PARKER, F. W., AND PIERRE, W. H. 1928 The relation between the concentration of mineral elements in a culture medium and the absorption and utilization of these elements by plants. *Soil Sci.* 25: 337-343.
- (30) SCHOLLENBERGER, C. J., AND DREIBELBIS, F. R. 1930 Effect of cropping with various fertilizer, manure, and lime treatments upon the exchangeable bases of plot soils. *Soil Sci.* 29: 371-394.
- (31) SCHOLLENBERGER, C. J., AND DREIBELBIS, F. R. 1930 Analytical methods in base exchange investigations on soils. *Soil Sci.* 30: 161-173.
- (32) SEARS, O. H. 1930 Relation of nitrates in soils to the response of crops to potash fertilization: I Factors contributing to the unproductiveness of "alkali" soils in Illinois. *Soil Sci.* 30: 325-347.
- (33) TRUE, R. H. 1922 The significance of calcium for higher green plants. *Science* (n. s.) 55: 1-6.
- (34) VOLK, N. J., AND TRUOG E. 1934 A rapid chemical method for determining the readily available potash of soils. *Jour. Amer. Soc. Agron.* 26: 537-546.
- (35) WHITTING, A. L., AND RICHMOND, T. E. 1921 Sweet clover for nitrate production. Ill. Agr. Exp. Sta. Bul. 233.



# A SIMPLE METHOD OF ESTIMATING EXCHANGEABLE CALCIUM AND OTHER BASES IN NON-CALCAREOUS SOILS

AMAR NATH PURI

*Irrigation Research Institute, Lahore (India)*

Received for publication January 9, 1935

The determination of exchangeable Ca in non-calcareous soils is very important because if this exchangeable base falls below a certain value Ca deficiency will result, necessitating liming. Apparently such estimations present no serious difficulties in the sense that, on account of the absence of  $\text{CaCO}_3$ , there are no complications introduced through solubility effects. Simplification of the technique, however, appeared feasible, and the present investigation was undertaken with that object in view.

Since Ca is precipitated quantitatively as Ca oxalate, it seemed reasonable to expect that if standard oxalic acid be added to soil in the presence of a reagent that would bring the exchangeable Ca into solution, the decrease in the concentration of oxalate ion would be equivalent to the amount of exchangeable Ca in the soil. A number of experiments were performed to study the conditions under which the complete precipitation of Ca takes place. These are discussed in this paper.

## EXPERIMENT

In order to standardize the working details, several preliminary experiments were carried out in which a heavy black cotton soil, possessing a high base exchange capacity, was used. The soil was first treated with 0.05 *N* HCl, to free it from carbonates and exchangeable bases, then leached with water. The soil still retained 8.8 m.e. of Ca per 100 gm. To 5-gm. portions of this soil increasing amounts of  $\text{Ca}(\text{OH})_2$  solution were added and left overnight. Next morning, standard oxalic acid solution was added to the suspension, and the total volume of the solution (without the soil) was made up to 150 cc. in every case. In one series, approximately 1 gm. of solid potassium acetate was added to each suspension; the second series was left as it was. The suspensions were left for 4 hours with occasional shaking and then filtered through a fluted filter. Seventy-five cubic centimeters of the filtrate was taken and titrated against standard  $\text{KMnO}_4$  solution. The decrease in the concentration of oxalate ion was reckoned equivalent to the total exchangeable Ca. The results given in table 1 show that the whole of the Ca is accounted for in the K acetate series, but a considerable amount was left in the soil when this reagent was not added.

In the next experiment, the precipitation of Ca oxalate was tried in the presence of 0.5 *N* acetic acid. The results given in table 2 show that the presence of acetic acid has practically no effect on the precipitation of exchangeable Ca by oxalic acid alone. If anything, the amount of Ca left in the soil is slightly more with acetic acid than without it.

TABLE 1

*Precipitation of exchangeable Ca as oxalate with and without K acetate*

All values in milliequivalents per 5 gm. of soil

Ca PRESENT	Ca FOUND WITHOUT K ACETATE	WITH K ACETATE
1.405	0.40	1.68
2.370	1.40	2.50
3.335	2.37	3.32
4.200	3.04	4.19
5.265	4.00	5.10

TABLE 2

*Precipitation of exchangeable Ca with oxalic acid in the presence of 0.5 N acetic acid*

All values in milliequivalents per 5 gm. of soil

Ca PRESENT	Ca FOUND
1.44	0.12
2.44	1.33
3.44	2.00
4.44	3.26
5.54	4.10

TABLE 3

*Precipitation of exchangeable Ca with oxalic acid in the presence of increasing amounts of acetic acid, with and without K acetate*

SOIL	STRENGTH OF ACETIC ACID	Ca PRESENT	Ca FOUND	
			With K acetate	Without K acetate
gm.	<i>N</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
0	0	3.82	....	3.82
0	0	3.82	....	3.78
5	0	4.26	4.18	3.13
5	0.05	4.26	3.82	2.91
5	0.01	4.26	3.98	3.10
5	0.2	4.26	3.63	2.97
5	0.5	4.26	3.45	2.86

Increasing concentrations of acetic acid were next tried both with and without K acetate. The results given in table 3 show that the greater the concentration of acetic acid, the smaller is the amount of exchangeable Ca precipitated. In the absence of the soil, however, the whole of the Ca is precipitated by oxalic acid, with or without acetic acid.

The failure of acetic acid to bring about the complete replacement of Ca in the soil is very interesting and most probably is due to the fact that Ca-oxalate cannot be precipitated completely unless the pH value of the solution is above 3.5. Since the soil with acetic acid and oxalic acid constitutes a system with a pH value less than 3.5, a part of the Ca oxalate dissolves and is again taken up by the soil with the liberation of oxalic acid, with the result that a part of the exchangeable Ca remains in the soil. In this connection a novel experiment was performed illustrating chemical reaction between two insoluble substances: 5 gm. of the acid treated soil was shaken for an hour with some Ca

TABLE 4  
*Decomposition of calcium oxalate by soil containing increasing amounts of calcium*

0.1 N Ca (OH) <sub>2</sub> ADDED TO 5 GM. OF SOIL	pH VALUE	0.1 N OXALIC ACID BROUGHT INTO SOLUTION	
		With acetic acid	Without acetic acid
cc.		cc.	cc.
0	4.52	10.7	8.1
7.84	5.28	9.6	3.1
15.68	6.28	5.2	0.5
23.52	8.58	4.4	0.3
31.36	9.53	3.6	0.5
39.20	10.20	2.9	0.4

TABLE 5  
*Precipitation of exchangeable Ca in the presence of increasing amounts of KOH*  
The soil contained 4.36 m.e. of exchangeable Ca

0.1 N KOH SOLUTION	CALCIUM PRECIPITATED
cc.	m.e.
0	3.05
10	3.35
20	3.58
30	3.84
40	4.20
50	4.32

oxalate suspended in 100 cc. of water. When the suspension was filtered, it was found to contain 8.1 cc. of 0.1 N oxalic acid, showing thereby that apparently insoluble soil colloids are capable of decomposing insoluble Ca oxalate, a feat characteristic of the so-called strong acids only. In the light of this experiment it is not difficult to understand the decomposition of insoluble calcium phosphate by an acid soil.

The decomposition of Ca oxalate was next tried with the same soil after the addition of increasing amounts of Ca(OH)<sub>2</sub>, both with and without acetic acid. The results given in table 4 show that in the presence of 0.5 N acetic acid, the soil is able to decompose calcium oxalate even when it is saturated with cal-

cium, pH 10. On the other hand in the absence of acetic acid the soil practically ceased to react with calcium oxalate when it contained enough Ca to give a pH value of 6.28.

Since the decomposition of calcium oxalate by the soil is mainly due to the low pH value of the reaction medium, this may not take place if the pH value of the soil be raised by the addition of alkali. This is illustrated in table 5, which records the results of an experiment in which 5-gm. portions of the acid treated soil were left with standard  $\text{Ca}(\text{OH})_2$  solution overnight. Next morning 10 cc. of *N* oxalic acid and increasing amounts of 0.1 *N* KOH were added and the total volume (without the soil) was made up to 150 cc. The suspension was shaken for an hour and filtered. Seventy-five cubic centimeters of the filtrate was titrated with permanganate as usual. It will be seen from table 5 that when the oxalic acid was half neutralized the whole of the exchangeable Ca was precipitated.

TABLE 6

*Precipitation of exchangeable Ca in the presence of increasing concentrations of potassium acetate*

The soil contained 4.4 m.e. of Ca per 5 gm.

SHAKING TIME	Ca FOUND K ACETATE IN 150 CC.								
	0 gm.	0.1 gm.	0.2 gm.	0.3 gm.	0.5 gm.	0.75 gm.	1.0 gm.	1.5 gm.	2.0 gm.
hours	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
1	2.98	3.28	3.30	3.40	4.06	4.32	4.38	4.36	4.39
2	3.04	3.04	3.22	3.44	3.98	4.28	4.37	4.37	4.47
3	3.06	3.06	3.24	3.44	3.85	4.34	4.45	4.35	4.41

In order to find the minimum quantity of potassium acetate required to bring about the complete precipitation of replaceable Ca by oxalic acid, 5-gm. portions of the soil containing 4.4 m.e. of Ca were shaken for varying lengths of time with oxalic acid in increasing strengths of potassium acetate, and Ca was determined as usual by the decrease in the concentration of oxalic acid. The results, given in table 6, show that the whole of the exchangeable Ca is precipitated as oxalate in 1 per cent solution (approximately 0.1 *N*) of potassium acetate by shaking for 1 hour.

The possibility of Mg being precipitated along with Ca was explored by precipitating Ca in the presence of increasing amounts of magnesium acetate solution. The results given in table 7 show that Mg is not precipitated under these conditions; hence, exchangeable Ca could be determined in soils containing fairly large amounts of exchangeable Mg.

#### DETAILED DESCRIPTION OF THE PROPOSED METHOD

Soil in 10 to 20-gm. lots is shaken for 1 hour with 100 cc. of 0.1 *N* oxalic acid in 0.2 *N* potassium or ammonium acetate. This solution can be prepared as a stock solution. After being shaken, the suspension is filtered through a



fluted filter paper, and 50 cc. of the filtrate is titrated with standard permanganate after the addition of  $\text{H}_2\text{SO}_4$  in the usual way. The total decrease in the concentration of the oxalate ion is equivalent to the exchangeable calcium in the soil.

Humus soils when treated with ammonium acetate and oxalic acid give a colored filtrate which cannot be titrated directly with permanganate. For such soils the method is modified as follows: 50 cc. of the filtrate is treated with 50 cc. of 0.1 *N*  $\text{CaCl}_2$  solution, which precipitates the remaining oxalic acid. The precipitate of Ca oxalate is filtered, washed, and ignited until all the Ca oxalate is converted into CaO. This CaO is mixed with a certain amount of impurities, such as the oxides of Fe and Al, derived from the soil and cannot be weighed directly. To the residue after ignition, therefore, is added a known amount of standard acid, which is back titrated with alkali.

The decrease in the concentration of the acid is equivalent to the CaO neutralized, which is equivalent to the oxalic acid remaining in the solution. This quantity when subtracted from the amount originally present in the solution, gives the decrease in the concentration of oxalic acid, which is equivalent to the exchangeable Ca in the soil. The results obtained by titrating the ignited

TABLE 7  
*Precipitation of Ca in the presence of increasing amounts of Mg*

Total volume—150 cc.

Mg present, gm.....	0	0.258	0.518	0.776	1.035	1.293	1.554	2.070
Ca found, m.e.....	3.88	4.00	3.98	3.90	3.94	3.90	3.90	3.95

residue with standard acid are practically the same as those obtained by dissolving it in acid, reprecipitating Ca as oxalate, and estimating it by titration with permanganate in the usual way.

In order to compare the method outlined in this paper with other standard methods of determining exchangeable Ca, ten soils were examined, the normal ammonium acetate and ammonium chloride leaching being used for comparison. In every case 10 gm. of the soil was leached with 1 liter of the solution. The results given in table 8 show good agreement except in the case of soil 3, the significance of which will be brought out later.

The difficulty of replacing all the calcium in a soil by simple leaching with a neutral salt or an acid is not generally recognized. This will be clear from table 9, in which are recorded the results of an experiment in which 10-gm. portions of a soil containing 66 m.e. of Ca per 100 gm. of soil were leached with different solutions in 100-cc. lots. Calcium was estimated in successive 500 cc. of the leachates. It will be seen that in almost every case even the fifth lot contains some Ca and the total amount obtained even by such prolonged leaching in several cases falls short of the value obtained by the proposed method. Table 9 also indicates the comparative efficiency of the various rea-

gents in bringing about the replacement of Ca. It will be seen that 0.5 *N* acetic acid is probably the least effective. The use of this reagent for estimating exchangeable bases in soils, as suggested by Williams,<sup>1</sup> cannot, therefore, be recommended in the light of these experiments. Exchange reactions being mainly ionic, the slowness of acetic acid is obviously due to its low ionization constant.

TABLE 8  
*Exchangeable Ca in soils determined by different methods*

SOIL NUMBER	pH	CLAY  <i>per cent</i>	EXCHANGEABLE Ca PER 100 GM.		
			Ammonium Acetate	Ammonium Chloride	Proposed method
			<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
3	7.64	63.8	53.8	53.1	59.6
6	5.29	31.6	5.1	4.9	5.4
9	5.76	22.8	3.8	4.45	4.6
12	5.84	14.8	3.6	3.95	3.2
14	5.37	31.5	2.8	3.75	5.0
15	7.71	27.6	13.0	13.90	12.0
18	5.79	25.1	4.0	4.30	3.6
20	5.64	15.1	3.1	1.80	2.2
22	6.85	17.8	7.85	8.10	8.5
23	7.41	11.8	8.20	9.05	9.0

TABLE 9  
*Replacement of Ca by leaching with different reagents compared with the proposed method*

METHOD	Ca IN SUCCESSIVE 500-CC. LEACHATES					
	1	2	3	4	5	Total
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
<i>N</i> ammonium acetate.....	59.75	1.8	0.3	0.65	0.15	62.65
0.2 <i>N</i> ammonium acetate.....	55.65	3.4	1.2	0.6	....	60.85
<i>N</i> ammonium chloride.....	61.6	2.35	1.6	0.2	1.3	66.05
<i>N</i> NaCl.....	59.9	2.5	1.55	0.8	0.5	65.25
0.2 <i>N</i> NaCl.....	44.95	7.4	3.85	2.25	....	58.45
<i>N</i> KCl.....	59.3	2.4	1.3	1.1	1.15	65.25
0.2 <i>N</i> KCl.....	54.0	4.65	1.5	0.65	0.8	61.6
0.05 <i>N</i> HCl.....	57.95	0.5	0.9	0.8	0.1	60.25
0.5 <i>N</i> Acetic acid.....	43.75	8.35	4.3	3.0	2.1	61.5
Proposed method.....	....	....	....	....	....	66.3

The difficulty of replacing exchangeable Ca is so much greater in the case of humus soils that it is practically impossible to replace the whole of the Ca with a reasonable amount of leaching. This will be clear from table 10, which

<sup>1</sup> Williams, Rice, 1928. The determination of exchangeable calcium in carbonate free soils. *Jour. Agr. Sci.* 18: 439.

records the exchangeable Ca in a number of humus soils by the proposed method and by leaching with *N* ammonium acetate in 100-cc. lots, Ca being determined in 500-cc. lots. As in every case a colored filtrate was obtained, the modified technique was used and Ca was determined both by titrating the CaO in the ignited residue (A) and by dissolving the residue in acid and reprecipitating Ca as oxalate, followed by filtration and titration with permanganate (B).

TABLE 10

*Exchangeable Ca in humus soils by the proposed method compared with N Ammonium acetate leaching*

SOIL NUMBER	LOSS ON IGNITION	EXCHANGEABLE Ca PER 100 GM.						
		In successive 500-cc. leachates					Proposed method	
		1	2	3	4	Total	A	B
	<i>per cent</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
404	35.9	54.2	8.75	2.35	1.50	66.8	66.5	67.6
405	9.4	17.8	2.5	0.6	0.25	21.15	28.0	29.4
247	46.3	78.3	20.5	10.4	3.15	112.35	114.0	....
390	27.5	49.8	6.15	2.30	1.05	59.30	61.8	63.3
345	41.2	53.15	7.10	2.45	1.25	63.95	67.8	68.2
397	29.0	36.8	5.4	2.05	0.3	44.55	49.0	50.3
398	27.2	36.65	4.05	1.15	0.25	42.10	50.1	50.6
333	31.3	61.1	11.8	5.1	1.6	79.60	86.0	86.8
334	16.0	33.9	4.25	1.95	0.2	40.30	46.8	48.2
236	33.6	58.9	10.1	3.55	1.85	74.40	81.0	81.4
237	10.8	35.75	5.1	2.9	0.5	44.25	45.4	46.8

TABLE 11

*Exchangeable bases present and found by the proposed method*

EXCHANGEABLE BASE	M.E. PER 100 GM.	
	Present	Found
Ca.....	33.8	34.6
Mg.....	10.5	11.0
Na + K.....	7.0	5.2

The difficulty of replacing exchangeable Ca by any of the usual reagents employed for this purpose and the ease with which this can be accomplished by precipitation *in situ* suggest a very simple method of estimating all the exchangeable bases in non-calcareous soils. The method is based on the fact that *all other bases except Ca are replaced by a single treatment with normal ammonium acetate*. The following is a detailed description of the method:

Twenty-five grams of soil is shaken for 1 hour, or left for 4 hours with frequent stirring, with 250 cc. of 0.05 *N* to 0.1 *N* oxalic acid in normal ammonium acetate. The suspension is then filtered through a dry filter paper. Fifty

to one hundred cubic centimeters of the filtrate is titrated with standard permanganate or precipitated with  $\text{CaCl}_2$ , if the filtrate is colored, as described in the foregoing. The total decrease in the concentration of oxalate ion is equivalent to the exchangeable Ca in 25 gm. of the soil. Another 100 to 150 cc. of the filtrate is evaporated to dryness in a porcelain dish and ignited to convert Na, K, and Mg acetates or oxalates into carbonates. The ignited residue is taken up with 50 per cent alcohol, which dissolves Na and K carbonates, leaving behind Mg carbonate. The alcoholic filtrate is evaporated to dryness and titrated for Na and K carbonates by first adding excess of standard acid. The residue of Mg carbonate is titrated separately by adding excess of standard acid, boiling, and back titrating with standard alkali. These titration values give the amount of exchangeable Na + K and of Mg per 10 gm. of soil for every 100 cc. of the filtrate.

The foregoing method was tested on an acid treated soil to which known amounts of Ca, Mg, Na, and K were added as hydroxides. The results given in table 11 show a good agreement between the bases present and those found by the proposed method.

#### SUMMARY

A simple method of estimating exchangeable Ca and other bases in non-calcareous soils is described. It consists in shaking a known weight of the soil with 0.1 *N* oxalic acid in *N* ammonium acetate. In this way the whole of the Ca is precipitated as oxalate, and the decrease in the concentration of the oxalate ion is equivalent to the exchangeable Ca in the soil.

Under the experimental conditions described, all the exchangeable bases other than Ca pass into solution as acetates or oxalate. A known volume of the filtrate is evaporated to dryness and ignited, when these bases are obtained as carbonates and are determined by titration with standard acid.

MISSOURI AGRICULTURAL EXPERIMENT STATION LIBRARY

# A DEVICE FOR MEASURING PRECIPITATION WATERS LOST FROM THE SOIL AS SURFACE RUNOFF, PERCOLATION, EVAPORATION, AND TRANSPIRATION

G. W. MUSGRAVE<sup>1</sup>

*U. S. Department of Agriculture, Bureau Chemistry and Soils*

Received for publication January 17, 1935

The investigations which are now in progress on the movement of surface waters and their effect upon the problem of conservation of both soil and water have pointed toward the need of certain types of studies. Among these is the need for specific information, developed under as nearly normal conditions of exposure as possible, upon the relationship of surface runoff to water absorption and retention by the soil. That portion of the precipitation which is retained by the soil under various conditions of treatment as well as for soils of various physical characteristics is water not only passed beyond the possibility of causing erosion, but further, is largely water which is of potential value to crop growth. The fact that many treatments may increase the absorption of precipitation waters is well known. The quantitative relationships between rate of precipitation, rate of infiltration, and rate of runoff are less well known. Such information is needed for soil series and types as well as for various conditions of treatment of each.

To be of practical use and true value any such quantitative measurements must be based upon soil of normal field structure, since a disturbance of such structure results in very abnormal infiltration rates. This fact has become recognized in the various improvements in design of lysimeters in recent years.

In many of the early established lysimeters either one or both of two serious defects existed:

- a) The soil was filled in after screening or other preparation such that original field structure was destroyed; and/or
- b) Free runoff of surface waters was not permitted.

Both of these conditions, of course, have the effect of increasing the quantity of water which passes through the soil profile, the result being not only to give abnormally high quantitative results but also to upset differential effects between treatments. Those soil treatments which normally would retard water absorption do not show a true relationship to other treatments under conditions in which all of the precipitation is retained upon the area of the lysimeter, thereby enforcing similar or nearly similar absorption rates.

<sup>1</sup> Scientist in Soil Erosion, Supt. of Soil Erosion Station Missouri Valley Loess Region and Supt. of Soil Erosion Station of Missouri-Iowa Brown Loam Region.

McCall and Bower (3) encased in tanks blocks of soil of undisturbed structure. These blocks were 3½ feet square by 4 and 6 feet deep, respectively. Corn was grown on the tanks, and tarred paper frames were used to cover the plant and protect from rainfall. Each tank was equipped with a syphon to maintain a constant groundwater table, and water losses from this table were measured in comparison with losses from an open water tank similarly equipped with a syphon and located nearby.

Duley (1) has described a type of lysimeter which permits the study of large sections of soil of undisturbed structure. This lysimeter consists of a heavy galvanized cylinder with removable bottom. A column of soil is trimmed to size and the cylinder placed over the column, the bottom fitted and the entire mass moved to the place of final installation. No provision for free surface runoff was made, although it appears that such could readily be permitted without fundamental change in design of the equipment.

Joffe (2) has described the Russian type of lysimeter which largely overcomes the two objections already enumerated. This type of lysimeter provides the essentials both of free runoff and soil of normal structure. It does not, however, permit the measurement of runoff in relation to percolation. Furthermore, as Joffe points out with reference to the relatively impervious B horizon, "the vertical movement of moisture becomes impeded and horizontal movement along this horizon sets in, a phenomenon to be reckoned with in lysimeter studies." Hence the percolation may not be quantitatively related to either precipitation or surface runoff where an impervious horizon is under study.

Weaver and Crist (4) have determined by direct measurement the loss of water from vegetation without disturbing the normal structure of the soil. For this purpose a cylinder 3 feet long and with an inner cross-sectional area of 1 square foot was forced over the grassy vegetation and into the soil, the exterior soil being pared away as the cylinder was forced downwards. These cylinders of soil were then removed and after being weighed were placed in a trench where the bottoms were sealed. The trenches were then filled with soil, and the surface sod was restored. Water losses over a 15-day period were calculated by weighing.

In order to provide a means of quantitative study of percolation and runoff in relation to rainfall the equipment described herein has been designed and constructed. Six lysimeters of this type have been in operation at the Soil Erosion Station at Temple, Texas, for approximately 4 years, and twelve of the same general type but with minor improvements have been in operation at the Clarinda Iowa Station for approximately 2 years. The general design, therefore, has been subjected to considerable practical experience with such satisfactory results that additional installations have lately been made.

The plan and elevation of the equipment is given in figure 1. The cylinders of this equipment as now installed are each 3 feet in diameter and 3 feet in depth, and contain nearly one ton of soil. They were filled with soil in practically undisturbed structural condition in the following manner: A suitable location was first selected, having uniform soil which was typical of the soil used in supplementary runoff experiments (in this case a Marshall silt loam having a surface horizon approximately 12 inches deep). The uniformity of the soil was determined by careful examination of the profile of a trench dug on four sides of the proposed location of the cylinder.

The cylinder was set in a vertical position by careful leveling and forced to its full length into the soil by means of three house-jacks actuated from above by suitably weighted scaffolding (pl. 1, fig. 1). Approximately 6,000 pounds of sand bags were required to supply the necessary weight for forcing this

cylinder into the 3-foot profile. During this operation a heavy iron ring was bolted securely approximately 4 inches above the base of the cylinder to maintain it as nearly as possible in a true circular form. While the cylinder was

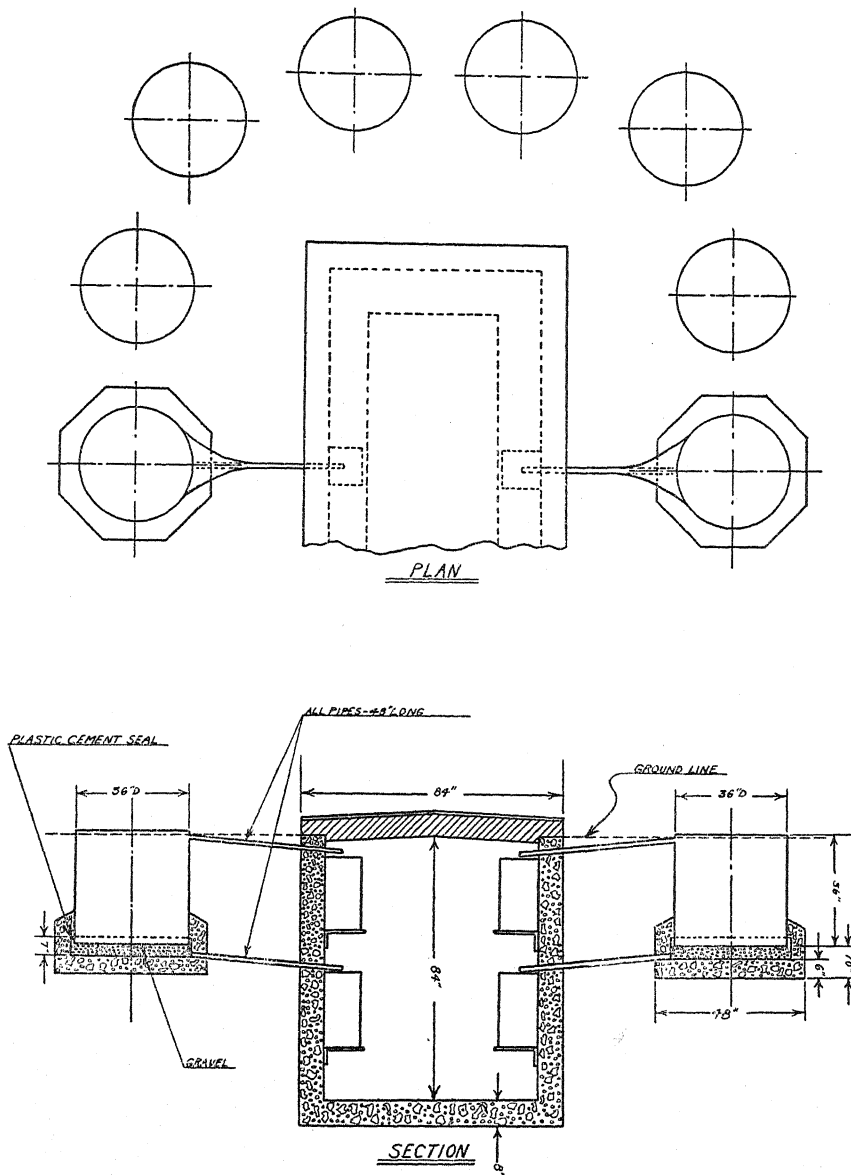


FIG. 1. PLAN AND ELEVATION OF EQUIPMENT USED IN THE MEASUREMENT OF SURFACE RUNOFF AND PERCOLATION FROM SOIL COLUMNS OF UNDISTURBED STRUCTURE

being forced downward the exterior soil was gradually removed to within a few inches of the bottom level of the cylinder. At the same time a series of six samples were obtained around the perimeter for each 6 inches of depth, making a total of 36 samples for each cylinder.

When the cylinder had been fully sunk excavation was continued on its exterior to a depth approximately 1 foot greater, and the lower hoop was removed, hooks were attached to the lower extremity (pl. 1, fig. 2), and the mass was supported on a hoist while the soil column was severed and carefully trimmed to an exact line coinciding with the plane of the lower end (pl. 1, fig. 3). When this operation is done on soil of this character (high silt or clay content and without rock or stone) at approximately optimum moisture content, there is no difficulty in retaining the entire mass of soil in the open-ended cylinder. At the same time the cylinders of soil were being prepared bases for their support in the final location were being constructed in the following manner: A reinforced concrete slab having a diameter 1 foot greater than that of the cylinder was first constructed. On this slab was then placed the pan which was to serve as the bottom of the completed cylinder. This pan, having a depth of 7 inches and diameter of 40 inches, was filled to a depth of 4 inches with coarse gravel which had been previously washed with hydrochloric acid and finally with distilled water. Above this layer of coarse gravel a layer of fine gravel similarly washed was then placed and tamped into position so that its surface was level. The pan itself was adjusted to have a 1-inch fall toward the outlet, which consisted of a 1-inch pipe set in the lower rim of the pan. A slight depression across the pan had been formed during its construction for the purpose of further aiding the movement of water to the outlet.

The cylinder of soil was then moved to the final location and placed carefully upon the pan. The joint between the pan and cylinder was first sealed by means of a preparation of asphalt, asbestos, and silica (pl. 2, fig. 1), after which a reinforced concrete shoulder was constructed in a manner to join firmly together the base and the cylinder as a single unit (pl. 2, fig. 2). The completed structure has such strength that the entire mass including pan and cylinder might be moved without breakage if desired, although this operation is, of course, not necessary (pl. 2, fig. 3).

The method of forcing the cylinder into the soil is such as to preserve the original vegetation and the original soil slope (pl. 3, fig. 1). Finally, however, the slope may be adjusted by fractions of an inch as may be necessary to duplicate precisely the slope in adjoining supplementary experiments.

In the completed installation (pl. 3, fig. 2) surface outlets care for the movement of surface runoff, which is carried into suitable containers in a nearby cellar. Likewise, percolate is piped from the gravel pan to suitable containers.

During the construction operation the cylinders of soil were weighed, the volume was measured, the moisture content was determined, and the apparent specific gravity of the mass was calculated. Detailed chemical and physical analyses of the soil have been made.

In the final installation the rain gage is installed in a manner such that its



top extends above the surface of the soil to the same height as that of the cylinders. Experience has demonstrated this to be necessary, inasmuch as records from rain gages with their tops extended 5 feet above the ground are rather consistently different from records of rain gages with their tops nearer the plane of the soil surface.

The data are handled in the following manner: The rainfall is carefully measured and calculated in terms of cubic centimeters per cylinder. Percolate is regularly measured and recorded as cubic centimeters, and in the surface runoff the soil and water are separated and each is separately calculated—the water in terms of cubic centimeters and the soil in terms of grams. Since over a period of time the cylinders of soil can neither continuously increase nor continuously decrease their content of soil water, it is feasible at the close of a selected period to calculate the disposition of the precipitation waters as they may occur in the form of evaporation and transpiration, as well as to

TABLE 1  
*Disposition of Precipitation Waters*  
May 1, 1933–May 1, 1934; Precipitation 25.15 inches

	FALLOW	FALLOW PLUS O.M.*	CORN	CORN PLUS O.M.*
Runoff, surface, <i>inches</i> .....	6.8170	6.3028	4.2729	2.5175
Percolation, surface, <i>inches</i> .....	4.1193	5.1770	0.7624	1.5122
Evaporation, surface, <i>inches</i> .....	14.2137	13.6702		
Evaporation plus transpiration, surface, <i>inches</i> ..			20.1147	21.1203

\* The fallow plus organic matter and the corn plus organic matter treatments each receive annually in early May an application of well-rotted stable manure at the rate of 16 tons per acre.

determine directly that amount lost as surface runoff and as percolate. This is done as follows:

On cropped cylinders:

$$E + T = P - (M + R)$$

where:  $E$  = Evaporation from the soil surface

$T$  = Transpiration from the plants grown in the cylinders

$P$  = Precipitation

$M$  = Percolate from the cropped cylinders

$R$  = Surface runoff from the cropped cylinders.

If the transpiration ratio for the type of plant is known, then the total transpiration for the season may be calculated and the soil evaporation may be determined from the equation:

$$E = P - (M + R + T)$$

On fallow cylinders:

$$E = P - (M' + R')$$

where:  $M'$  = Percolate from the fallow cylinders, and  
 $R'$  = Surface runoff from the fallow cylinders.

A simple total of the results for a calendar year from triplicate treatments is given in table 1.

There are at present in operation at the Soil Erosion Experiment Station in Iowa 24 units providing a total of 8 different treatments, each in triplicate and including two different soil types which receive corresponding applications of organic matter. The detailed data from this study are being reported separately.

A number of special advantages are found in this equipment whether its primary purpose be erosion research or whether for the usual lysimeter studies. For the latter purpose normal percolation rates are provided by this type of installation, whereas in the more commonly used type of lysimeter abnormal percolation occurs. This is due to the fact that where all of the precipitation waters are forcibly retained upon the soil surface such waters must ultimately enter into the soil, enforcing a rate of percolation in excess of that occurring under corresponding field conditions. Such differential effects are particularly pronounced in the case of those treatments which have a deflocculating effect upon the soil. In the Russian type of lysimeter, where free surface runoff is permitted, percolation rates for permeable soils are probably close to normal. In the case, however, where a relatively impermeable horizon intervenes there is no surety in the Russian type lysimeter that water from outside of the measured area may not enter into the measurement of the percolation.

Both the Russian type and that type of lysimeter described in the foregoing have the advantage of permitting studies on soil of undisturbed structure. In many types of studies it is very desirable to be able to relate quantitatively percolation and surface runoff to the precipitation. This advantage, as well as that of the indirect calculation of vapor losses, is obvious, and the equipment described is adaptable to the purpose.

#### REFERENCES

- (1) DULEY, F. L. 1925 A movable lysimeter for soil studies. *Soil Sci.* 20: 465-471.
- (2) JOFFE, J. S. 1932 Lysimeter studies: I. Moisture percolation through the soil profile. *Soil Sci.* 34: 123-143.
- (3) MCCALL, A. G., AND BOWER, H. J. 1911 A preliminary report on a field study of soil moisture. *Jour. Amer. Soc. Agron.* 3: 72-76.
- (4) WEAVER, J. E., AND CRIST, J. W. 1924 Direct measurement of water loss from vegetation without disturbing the normal structure of the soil. *Ecology* 5: 153-170.

#### PLATE 1

FIG. 1. Method of sinking cylinder into selected soil area. Jack screws were used for this purpose to give a slow, even movement without jarring the soil column. The cylinder was maintained exactly perpendicular throughout the operation.

FIG. 2. Two cylinders sunk to full depth, one of which has hooks attached ready for fastening to hoist.

FIG. 3. Gravel pan in position upon base. Note cylinder of soil on hoist ready to be moved into position upon base.

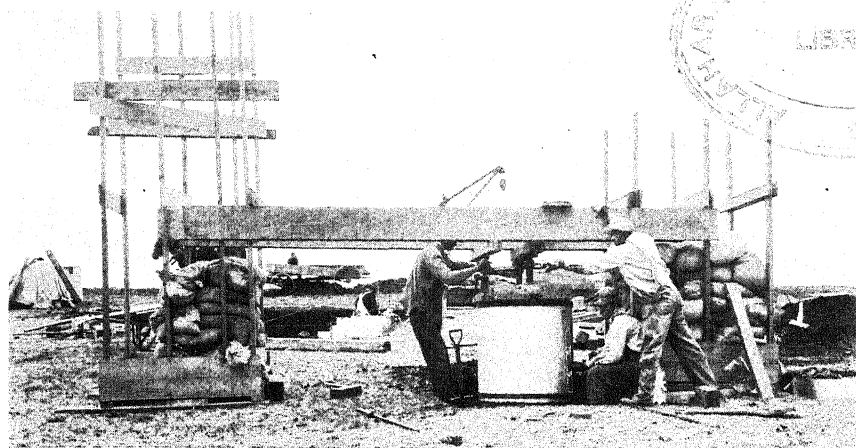


FIG. 1

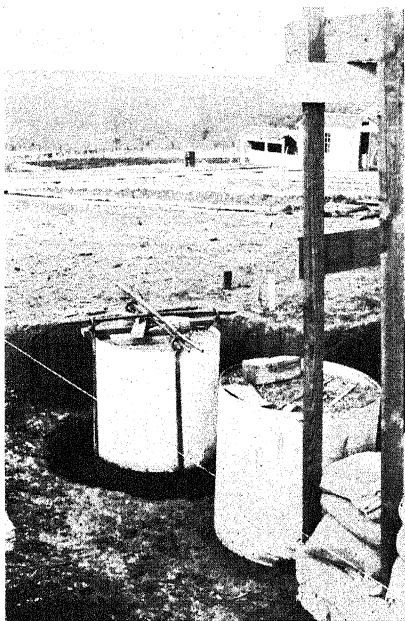


FIG. 2

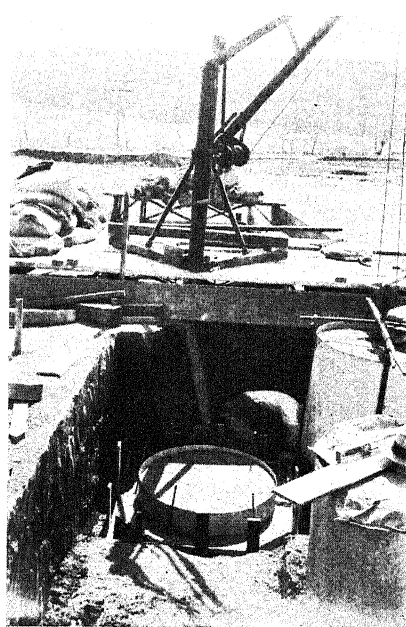


FIG. 3

## PLATE 2

FIG. 1. The cylinder in position upon the gravel pan and the operation of sealing a joint between the pan and cylinder with a preparation of silica, asphalt, and asbestos.

FIG. 2. Reinforcement in position for constructing concrete shoulder about base of cylinder and including pan. Also a view of one such base complete.

FIG. 3. Four cylinders in position, with the completed base.

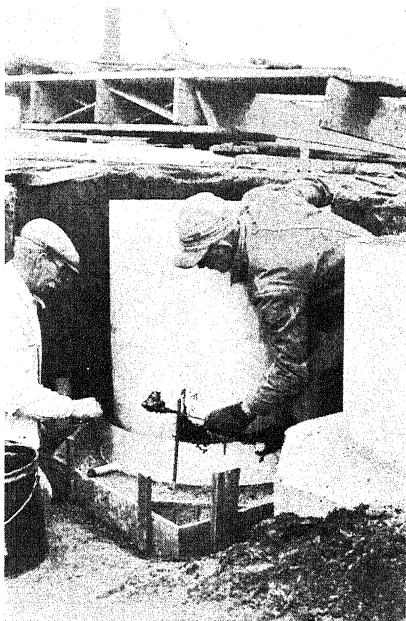


FIG. 1

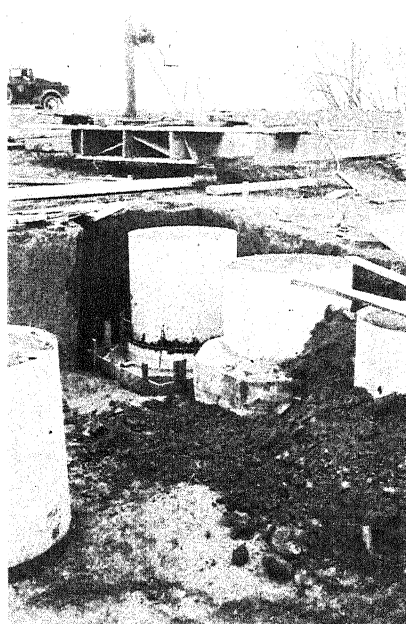


FIG. 2



FIG. 3

## PLATE 3

FIG. 1. Undisturbed condition of soil in cylinder after being sunk to its full depth. The original vegetation and the original soil slope remain.

FIG. 2. Cylinders spaced equi-distant from one another and from central cellar. (a) outlet pipe for surface runoff; (b) rain gage; (c) cellar housing measuring equipment for runoff and percolate.

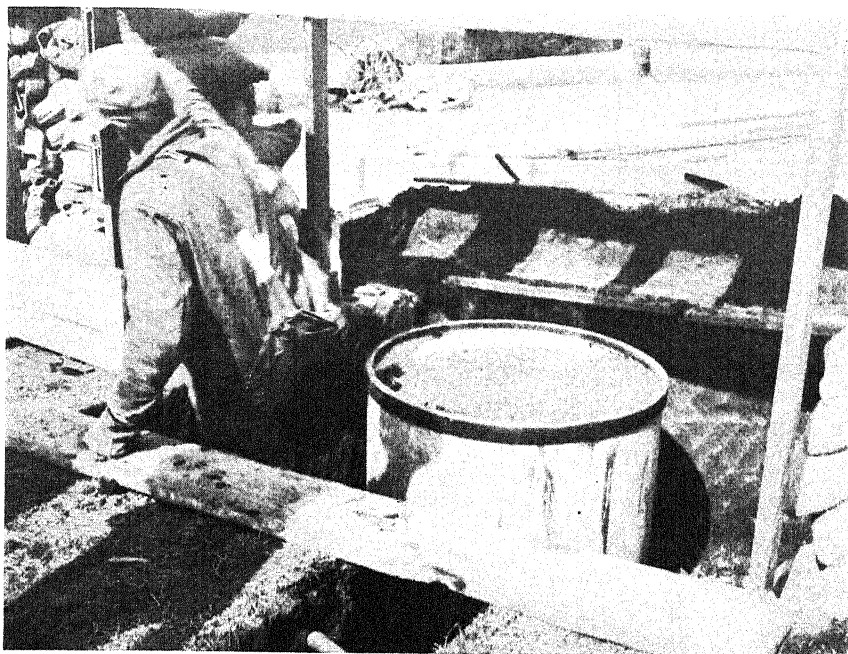


FIG. 1

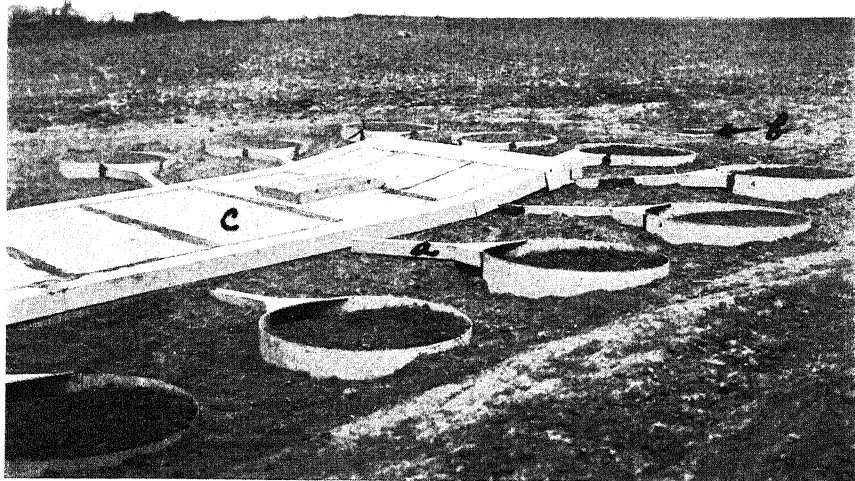


FIG. 2





## SORPTION OF LIQUIDS BY SOIL COLLOIDS: II. SURFACE BEHAVIOR IN THE HYDRATION OF CLAYS

L. D. BAVER AND HANS WINTERKORN<sup>1</sup>

*Missouri Agricultural Experiment Station<sup>2</sup>*

Received for publication February 2, 1935

In previous investigations (14) the authors have shown that the sorptive behavior of different soil colloids is related to the structure of the colloidal complex, to the amount and nature of the ions adsorbed on the surface, and to the electrical properties of the molecules of the sorbed liquid. It is the purpose of this paper to discuss the rate of water sorption by colloidal clays and such properties of clay-water systems as viscosity, charge, hygroscopicity, heat of wetting, and swelling, in order to permit a clearer concept of the rôle of surface behavior in the hydration of colloids.

### EXPERIMENTAL PROCEDURE

Water sorption and swelling were measured as discussed in Part I (14). Viscosities were determined with a special form of Oswald viscosimeter which permitted measurements in a closed system at higher temperatures. Preliminary observations showed no influence on the viscosity data by pressure variations within the systems from  $\frac{1}{2}$  to 2 atmospheres. Heat of wetting data were obtained with a Bunsen ice calorimeter. The contraction of the ice-water system was measured in a horizontal capillary which was installed at such a relative height to the bulk of the water and mercury as practically to eliminate any movement of the mercury due to melting or freezing of water induced by either pressure or suction. The reproducibility of the caloric data was within 5 per cent. The clays were pulverized, dried for 3 days at 110°C., and then kept over  $P_2O_5$ . Before being placed in the ice calorimeter they were cooled for an hour in an ice-water bath. Hygroscopicities were measured as usual over  $H_2SO_4 - H_2O$  mixtures. The charge and dispersity data are those reported by Lutz (10).

### DISCUSSION OF RESULTS

*The rate of water sorption.*—The rates of water intake by different colloidal systems are shown in tables 1, 2, and 3. The data in table 1 point out quite

<sup>1</sup> Assistant Professor and Research Chemist, respectively.

<sup>2</sup> Joint contribution from the department of soils, University of Missouri, Columbia, Missouri, and the Missouri State Highway Department, Jefferson City, Missouri.

Published with the approval of the director of the Missouri Agricultural Experiment Station as Journal Series Paper No. 393.



## SORPTION OF LIQUIDS BY SOIL COLLOIDS: II. SURFACE BEHAVIOR IN THE HYDRATION OF CLAYS

L. D. BAVER AND HANS WINTERKORN<sup>1</sup>

*Missouri Agricultural Experiment Station<sup>2</sup>*

Received for publication February 2, 1935

In previous investigations (14) the authors have shown that the sorptive behavior of different soil colloids is related to the structure of the colloidal complex, to the amount and nature of the ions adsorbed on the surface, and to the electrical properties of the molecules of the sorbed liquid. It is the purpose of this paper to discuss the rate of water sorption by colloidal clays and such properties of clay-water systems as viscosity, charge, hygroscopicity, heat of wetting, and swelling, in order to permit a clearer concept of the rôle of surface behavior in the hydration of colloids.

### EXPERIMENTAL PROCEDURE

Water sorption and swelling were measured as discussed in Part I (14). Viscosities were determined with a special form of Oswald viscosimeter which permitted measurements in a closed system at higher temperatures. Preliminary observations showed no influence on the viscosity data by pressure variations within the systems from  $\frac{1}{2}$  to 2 atmospheres. Heat of wetting data were obtained with a Bunsen ice calorimeter. The contraction of the ice-water system was measured in a horizontal capillary which was installed at such a relative height to the bulk of the water and mercury as practically to eliminate any movement of the mercury due to melting or freezing of water induced by either pressure or suction. The reproducibility of the caloric data was within 5 per cent. The clays were pulverized, dried for 3 days at 110°C., and then kept over  $P_2O_5$ . Before being placed in the ice calorimeter they were cooled for an hour in an ice-water bath. Hygroscopicities were measured as usual over  $H_2SO_4 - H_2O$  mixtures. The charge and dispersity data are those reported by Lutz (10).

### DISCUSSION OF RESULTS

*The rate of water sorption.*—The rates of water intake by different colloidal systems are shown in tables 1, 2, and 3. The data in table 1 point out quite

<sup>1</sup> Assistant Professor and Research Chemist, respectively.

<sup>2</sup> Joint contribution from the department of soils, University of Missouri, Columbia, Missouri, and the Missouri State Highway Department, Jefferson City, Missouri.

Published with the approval of the director of the Missouri Agricultural Experiment Station as Journal Series Paper No. 393.

clearly that the sorption of water by Li- and Na-saturated colloids is a more complex phenomenon than in the case of the K-, Ba-, Ca-, and H-systems. Sorption by the latter systems was 70-75 per cent complete within 1 minute and 85-90 per cent finished in 10 minutes. The pores were filled with easily expressible free water. The sorption of water by the Li- and Na-clays was not complete after 3 days. Of the total amount taken up during that time only 15 per cent was imbibed during the first minute and 22 per cent during the first 10 minutes. After about 24 hours the colloids began to disperse in the sorbed water and to diffuse through the porous filter plate. Consequently,

TABLE 1  
*Rate of water intake by Putnam colloid saturated with different cations*

TIME	WATER INTAKE PER GRAM COLLOID					
	Li*	Na*	K	Ba	Ca	H
<i>minutes</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>
1	0.960	0.810	1.120	1.344	1.362	1.330
5	1.195	1.020	1.230	1.480	1.540	1.506
10	1.360	1.200	1.284	1.526	1.624	1.566
20	1.615	1.490	1.316	1.564	1.678	1.588
30	1.765	1.555	1.326	1.584	1.704	1.608
120	.....	.....	.....	1.634	1.778	1.676
150	2.575	2.255	1.372	.....	.....	.....
1080	.....	.....	.....	1.688	1.888	1.780
1140	4.130	3.700	1.456	.....	.....	.....
1200	4.195	3.725	1.458	.....	.....	.....
1440	4.440	3.940	1.464	1.750	1.908	1.790
1550	4.510	3.975	.....	.....	.....	.....
4050	6.125	5.240	.....	.....	.....	.....
4320	6.225	5.270	.....	.....	.....	.....
Pore space, cc./gm.....	1.250	1.250	0.960	0.900	1.000	0.98
Swelling, cc./gm.....	4.975	4.020	0.504	0.850	0.908	0.81

\* The end values for the Li- and Na-collids are somewhat too low, since diffusion of these colloids through the porous filter plate started at about 24 hours. Sorption of water resulted in complete dispersion.

the end values for sorption are undoubtedly too low. It should be noted that although suspensions of Li-, Na-, and K-clays are dispersed to approximately the same extent, the K-saturated systems take up water in a similar manner to those saturated with H, Ba, and Ca ions. The data in table 2 show that although the amount of water sorbed by different H-clays varies with the nature of the colloid, the rates of sorption are of the same order of magnitude.

Sorption studies with colloidal bentonite systems showed (table 3) that the rate of water intake was much slower than with clays but that sorption extended over a much longer period of time. The quantity of water imbibed per gram of bentonite was much greater than per gram of clay. Equilibrium

with clay systems was obtained within 1 to 3 days; bentonite, however, continued to sorb small amounts of water after 5 to 7 days. All bentonite systems assumed a jelly-like consistency during the process of imbibition as compared with the dispersed condition of Li- and Na-clays and the seemingly granular nature of the K-, Ca-, Ba-, and H-clays. With the clay systems, the K-satu-

TABLE 2  
*Rate of water intake by various colloidal clays saturated with hydrogen ions*

TIME	WATER INTAKE PER GRAM COLLOID			
	Lufkin	Wabash	Susquehanna	Cecil
<i>minutes</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>
1	1.56	1.249	1.212	1.106
5	1.64	1.520	1.382	1.154
10	1.68	1.554	1.418	1.168
30	1.72	1.618	1.490	1.186
60	1.76	1.640	1.526	1.206
180	1.80	.....	1.578	1.234
1140	....	1.828	1.666	1.294
1440	2.00	1.838	1.666	1.294
Pore space cc./gm.....	0.82	0.90	1.10	1.24
Swelling cc./gm.....	1.18	0.938	0.566	0.054

TABLE 3  
*Rate of water intake by bentonite saturated with various cations*

TIME	WATER INTAKE PER GRAM BENTONITE					
	Li	Na	K	Ba	Ca	H
<i>minutes</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>
10	0.820	0.970	1.525	2.895	.....	2.645
20	1.190	1.310	.....	2.975	2.985	2.730
30	.....	.....	.....	3.015	3.025	2.765
60	1.910	2.090	2.625	3.085	.....	2.830
120	2.640	2.860	3.315	.....	3.215	.....
1440	7.430	7.695	7.145	3.475	.....	3.210
4320	11.170	11.290	9.055	3.830	3.920	3.570
5760	12.125	12.280	9.755	3.900	4.000	3.650
Pore space cc./gm.....	1.350	1.200	1.200	1.400	1.500	1.450
Swelling cc./gm.....	10.775	11.080	8.555	2.500	2.500	2.200

rated colloid behaved like the divalent clays; with bentonite, the Li, Na, and K ions exerted similar effects upon the sorption of water.

The differences in the rates and amounts of water sorption by these various colloidal systems indicate that the structure of the particles and the nature and activity of the colloidal surfaces must play important rôles in this type of

hydration. The significance of these results will be more thoroughly discussed under the subject of swelling.

*Hydration of clays.*—It is known from fundamental colloid chemistry that charge and hydration are the two factors governing the behavior of colloidal suspensions. For truly non-hydrated suspensoids (gold sols), charge plays the predominant rôle; for hydrated emulsoids (gelatin sol), hydration is more important. Experimental data have proved that colloidal aluminosilicates have properties common to emulsoids and suspensoids. The hydrophilic character of aluminosilicates is usually more pronounced the higher the  $\text{SiO}_2$ -sesquioxide ratio of the colloid; colloids with a low ratio tend to have hydrophobic characteristics. It should be expected that in highly hydrated aluminosilicate systems the influence of charge, as derived from the zeta-potential, on dispersion and the properties of the system relating thereto will be small as compared with the effect of the hydration factor. Consequently, in highly hydrated bentonite systems where the diffuse electrical double layer is undoubtedly thicker than in the less hydrated clays, the nature of the exchangeable cations in the somewhat mobile outer layer should not have such pronounced effects on dispersity. Moreover, the influences of the ions in the outer layer on the hydration of bentonite and clay surfaces should not be expected to be exactly similar. The experimental results of Lutz (10) and Marshall (11) on the charge of colloidal particles and dispersity as summarized in table 4 indicate quite clearly such differences in the effects of the exchangeable cations on clays and bentonites. It should be noted that the stability of the bentonite sols as measured by their degree of dispersion is nearly the same, irrespective of the nature of the ion on the exchange complex. Ca-, Ba-, and H-bentonites are as stable as the Li-, Na-, and K-systems. Only the Li-, Na-, and K-Putnam clays are permanently stable; the H-, Ca-, and Ba-clays undergo slow coagulation. The bentonites are from 5 to 7 times more highly hydrated than the various Putnam clays.

These data also show that the effect of the zeta-potential of different clays on their stability is determined to a large extent by the degree of hydration of the clay. For example, the potentials of the Davidson and Putnam colloids that are saturated with the alkali cations are practically the same. The Davidson colloids, however, flocculate rapidly, whereas the Putnam systems are stable. Undoubtedly as the degree of hydration of the surface increases the probability of adhesion for any given potential becomes smaller.

Many data have been assimilated in this study to show the differences in hydration of the various colloidal systems. Relative hydration of these colloids has been approached from the points of view of the adsorption of water molecules from the vapor phase (hygroscopicity), the adsorption or orientation of water molecules in the presence of an excess of water (relative viscosity), the intake of water from a free water surface (sorption and swelling), and the energy relationships associated with the wetting of a dry surface (heat of wetting).

The relative hydration of each of the different colloidal suspensions was calculated by means of the modified Einstein equation

$$\eta_r = \frac{1 + 2.5\phi}{1 - \phi}$$

where  $\eta_r$  = relative viscosity =  $\frac{\text{viscosity of suspension}}{\text{viscosity of water}}$

$\phi$  = volume in per cent of suspended particle with hydration hull.

Subtraction of the volume of the solid soil particle from  $\phi$  gave the amount of hydration. It was fully realized that, in view of the theoretical incompleteness of the Einstein formula as well as the increase in viscosity due to aggregation phenomena, the evaluation of the viscosity data in terms of hydration of the colloidal particle must be made with proper interpretations. It is believed, however, that if suspensions with equal dispersions are used the hydration values calculated from viscosity measurements will give satisfactory comparative data as to the amount of water bound to the colloidal surfaces.

Data relative to the hydration of several colloidal suspensions are summarized in tables 4, 5, and 6. The hydration values in table 4 show that colloidal bentonite suspensions are much more highly hydrated than colloidal clays. These results also show that flocculation phenomena may lead to misinterpretation of the viscosity measurements in terms of hydration, since the flocculated Davidson colloids exhibit higher hydration than the Putnam colloids. Other hydration studies such as swelling and hygroscopicity show, without doubt, that the Putnam clay systems are more highly hydrated. The similarity in the hydration of the H-, Ca-, and Ba-Putnam clays and of the Li- and Na-clays is due to the slow coagulation of the former.

The values in tables 5 and 6 indicate the effect of exchangeable cations on the hydration of Putnam and Wabash clays. It is seen in the case of the Putnam system that the ratio of hydration in an excess of water (from viscosity measurements) to that in an atmosphere of water vapor (hygroscopicity over 30 per cent  $\text{H}_2\text{SO}_4$ ) is almost constant for all ions.

The colloid appears to be about 30 times more hydrated in suspension. The hygroscopicity data, obtained by the common procedure of keeping the clay for 3 days in a dessicator over 30 per cent  $\text{H}_2\text{SO}_4$ , obviously do not represent true equilibria. This has already been shown by Deluc (3), and has been emphasized by Katz (8). Therefore, it cannot be decisively concluded from these data that only about one-thirtieth of the water attracted by a suspended colloid is held by a force greater than the avidity of 30 per cent sulfuric acid for water. The constancy of the hydration-hygroscopicity ratio rather points to an identity of the water-binding forces for both phenomena. The lower speed of water adsorption from an atmosphere can easily be conceived as being due to the low concentration of water molecules in the vapor and the resulting small number of those striking the colloidal surface per unit time.

Since a certain time element is needed for the orientation and binding of these water molecules there seems to be a greater probability for the orientation of relatively slow associated water molecules than for the orientation of the faster  $H_2O$  molecules from the atmosphere during their relatively small striking time.

Hydration as calculated from the viscosity of aqueous suspensions is related to the energy of adsorption as measured by the heat of wetting. For the Putnam colloid the hydration-heat of wetting ratio is about 0.43 for Li-,

TABLE 4  
*Relation of charge and hydration in different colloidal systems*

COLLOIDAL SYSTEM	ZETA-POTENTIAL (LUTZ-REITEMEIER)	WATER OF HYDRATION* (WINTERKORN) (LUTZ)	DISPERSITY	
			Flocculation time (Lutz)	Particles <100 m $\mu$ (Marshall)
	<i>millivolts</i>	<i>cc./gm.</i>		<i>per cent</i>
H-Davidson	36.8	6.66†	1 min.	
Li-Davidson	40.5	9.01	2 min.	
Na-Davidson	39.4	8.06	2 min.	
K-Davidson	37.9	11.41	2 min.	
Ca-Davidson	36.3	5.11	1 min.	
Ba-Davidson	35.3	5.76	1 min.	
H-Putnam	36.3	5.20	3 days	37.4
Li-Putnam	40.3	5.25	Stable	60.1
Na-Putnam	38.5	5.25	Stable	62.2
K-Putnam	38.7	4.07	Stable	56.3
Ca-Putnam	35.0	5.20	3 days	4.9
Ba-Putnam	32.6	5.20	3 days	24.4
H-Bentonite		35.00	Stable	34.0
Li-Bentonite		28.40	Stable	37.8
Na-Bentonite		24.10	Stable	35.2
K-Bentonite		21.30	Stable	35.7
Ca-Bentonite		24.20	Stable	31.2
Ba-Bentonite		34.00	Stable	31.9

\* From viscosities.

† Partly flocculated.

Na-, and K-systems, even though the K ion causes a lower heat of wetting and a lower viscosity. This ratio is 0.38 for the H, Ca, and Ba ions. The data strongly suggest that this hydration is a function of the energy of adsorption. If the ratio of swelling to heat of wetting is considered, it is observed that this value for H-, K-, Ca-, and Ba-systems is about 0.06; that for the Li- and Na-colloids is around 0.43. Swelling water in the latter systems approaches the amount of hydration calculated from the viscosity of the colloids in aqueous suspension. This should be expected from the aforementioned behavior of these clays in the sorption apparatus.



In the case of the Wabash colloid, which contains a considerable amount of organic matter, the hydration-heat of wetting ratio of the Ca- and Ba-systems is of the same order as the Putnam clays. The Li-, Na-, and K-saturated colloids, however, exhibit a much greater hydration as compared with the heat of wetting, causing the hydration-heat of wetting ratio to be higher.

TABLE 5  
*Hydration of Putnam colloid*

COLLOIDAL PROPERTY	NATURE OF CATION					
	H	Li	Na	K	Ca	Na
pH.....	4.1	7.61	7.66	7.32	6.96	6.86
Hydration*, cc./gm.....	5.20	5.25	5.25	4.07	5.20	5.20
Swelling, cc./gm.....	0.81	4.97	4.02	0.50	0.91	0.85
Heat of wetting, cal./gm.....	13.6	12.0	12.0	9.5	15.0	13.9
Swelling						
Heat of wetting	0.06	0.414	0.335	0.053	0.061	0.061
Hydration*						
Heat of wetting	0.382	0.437	0.437	0.429	0.382	0.381
Hydration*						
Hygroscopicity (30 per cent H <sub>2</sub> SO <sub>4</sub> )	28.65	30.65	31.75	31.9	31.9	29.9

\* From viscosities.

TABLE 6  
*Hydration of Wabash colloid*

COLLOIDAL PROPERTY	NATURE OF CATION					
	Li	Na	K	Ba	Ca	H
Hydration*.....	7.39	7.45	7.03	6.67	6.74	Floc.
Swelling.....	3.10	3.73	0.55	0.74	0.79	0.94
Heat of wetting.....	11.4	11.6	8.9	14.9	15.3	13.9
Hydration*						
Heat of wetting	0.648	0.643	0.789	0.448	0.440	.....
Swelling						
Heat of wetting	0.272	0.322	0.062	0.052	0.049	0.067

\* From viscosities.

This greater hydration is undoubtedly due to the influence of the alkali ions on the organic colloids present.

Apparently there are at least two ways in which water can be associated with colloidal particles, not taking into consideration mechanically occluded water. Water molecules may be oriented at the surface as a result of the electrical properties of both the liquid and the surface. Water may also be adsorbed because of osmotic effects, as described by Proctor, Proctor and Wilson, and Mattson. The first process is associated with the release of an

appreciable amount of heat and will be referred to as "hydration." The osmotic type of hydration does not take place with the liberation of measurable quantities of heat. It apparently plays a significant part in the hydration of the alkali-saturated organic colloids in the Wabash clay. This osmotic hydration is not restricted to organic colloids but is also found, as Mattson (12) has shown, in highly hydrated aluminosilicates such as bentonites.

The observations of Marshall (11), Lutz (10), Winterkorn (14), Janert (6), Mattson (12), and others suggest that the water association with common colloidal clays is principally due to hydration; that of organic colloids and bentonites also includes an appreciable amount of osmotic hydration. Hydration can be pictured as oriented adsorption of water molecules at the surface of the colloid and around the ions whereby the exchangeable ions are found either in conformity with the surface or very close to it.

In the osmotic type of hydration the hydrated ions surround the hydrated surface in a diffuse layer. These ions keep within a distance from the surface in which the mean osmotic force is in equilibrium with the mean electric attraction due to the different charges of the colloidal surface and the exchangeable ions. The apparent volume of the colloidal particle is then defined by the extent of the ionic atmosphere. The free water in which the cations are dispersed is naturally an integral part of the apparent volume of the swollen particle, and since the diffuseness of the double layer is a function of the osmotic pressure of the cations this type of swelling has been termed "osmotic." It will be understood now that this type of swelling is not directly connected with any appreciable energy change in contrast to hydration. The diffuseness of the ionic atmosphere is also a function of the electric structure of the colloid surface. There seems to be reason to believe that a study on the polarizing effect of the crystal surfaces of the different soil colloids will throw light upon the problem of the different behavior of bentonites and clays.

It can be stated, therefore, in colloid chemical terms that the nature of the inner layer and its effect on adsorption of ions and water molecules determine to a great extent the character and amount of hydration in aqueous clay systems. The kind of ion adsorbed on the surface plays an important rôle in hydration as well as in the osmotic type of hydration. This rôle, however, is probably not so simple and well-defined as to make the heat of wetting of clays always a definite fraction of the heat of hydration of the ions in the surface. These relationships will be discussed later in this paper.

In order to obtain information concerning the force with which water is oriented or held around a colloidal particle, the effect of temperature on the viscosity and hygroscopicity of colloids was studied. The data in tables 7 and 8 show that an increase in temperature, which correspondingly causes an increase in the kinetic energy of the water molecules, produced marked decreases in the hydration of the particles as calculated from viscosity and hygroscopicity data. At temperatures close to the boiling point of water the colloid is only about 50 per cent as highly hydrated as at room tempera-

ture. This decrease in hydration was a uniform function of increasing temperature, since there were no abrupt changes in temperature-hydration curves. The hygroscopicity data show that increasing the temperature from 30° to 40°C. caused over a 50 per cent decrease in the amount of water ad-

TABLE 7  
*Hydration\* of Putnam and Wabash colloids as affected by temperature*

TEMPERATURE	HYDRATION, CC. H <sub>2</sub> O PER GRAM COLLOID					
	Li	Na	K	Ca	Ba	H
<i>Putnam colloid</i>						
°C.						
30	5.25	5.25	4.07	9.75	5.04	5.20
50	3.73	4.56	3.56	3.90	3.73	3.52
70	2.52	2.53	2.34	1.98	2.87	2.16
99	2.34	2.52	2.16	0.86	2.16	2.70
<i>Wabash colloid</i>						
30	7.39	7.45	7.03	6.74	6.67	17.95
50	6.37	6.29	6.22	6.14	6.22	16.08
70	5.01	5.09	4.75	6.44	4.40	14.79
99	3.86	3.67	3.39	7.10	3.39	9.70

\* From viscosities.

TABLE 8  
*Water adsorption by different aluminosilicates as a function of temperature*  
Vapor pressure = 30 mm. Hg, relative humidity = 94 per cent at 30°

COLLOID	H <sub>2</sub> O ADSORBED			
	Temperature			
	30°	40°	50°	80°
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
H-Bentonite.....	32.7	13.0	7.51	2.12
H-Putnam.....	25.8	10.8	5.7	2.3
H-Davidson.....	21.4	3.5	2.6	1.2
H-Permutite.....	28.4	16.9	4.9	3.1
Strength of H <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O mixture used to maintain constant humidity, <i>per cent</i> .....	10	41.5	52.75	68.75

sorbed, even though the water vapor pressure was held constant. These results, in conformity with the previous discussions on hygroscopicity and hydration, indicate that the water molecules in the outer layers of the water shell of a soil colloid in aqueous suspension are held by relatively small forces, smaller than the water attractive forces of the sulfuric acid used in the hydro-

scopicity determinations. The data for the hydration as calculated from the viscosities were somewhat affected by coagulation phenomena at the higher temperatures, but not sufficiently to account for the characteristic difference between the temperature function of hydration and that of hygroscopicity. This difference may be due in part to different equilibria between the clay, on one hand, and molecular or associated water, on the other.

*Swelling of soil colloids.*—In Part I of this study the swelling of soil colloids has been considered as the difference between the sorption of water and of an inactive, non-polar liquid such as  $\text{CCl}_4$ . It is realized, in the light of the different physical behavior of the swollen systems, that the apparent swelling does not represent any one specific physical or physicochemical phenomenon. In the hope of clarifying many of the existing and apparently contradictory explanations of swelling, the data obtained in this study on the swelling of colloidal aluminosilicates will be discussed from the points of view of the different interpretations usually given to the swelling process.

At the end of the last century the botanists defined "swelling" as the intake of liquid by a solid body, whereby the volume of the body is enlarged and its cohesion diminished without loss of its apparent microscopic homogeneity. Capillary intake is sharply distinguished from swelling. In more recent times a greater emphasis has been placed on the forces acting in the swelling process, and the meaning of "swelling" has been widened to cover such amounts of pore-filling liquids as have lost their free mobility as a result of forces acting at or within the surface of the porous material. Although practically all substances that possess the capacity to swell also have the common property of a large existing or potential surface, the different physicochemical characteristics of the swelling solids as well as of the liquid play exceedingly important parts in the process, thereby making it extremely difficult to explain swelling by any single physical or physicochemical phenomenon. The fact that liquids used in swelling may consist of (a) associated water-like molecules with large dipole moments, (b) molecules unlike water but with dipole moments, and (c) organic liquids without dipole moments suggests at least three different types of swelling. These are (a) polar liquids bound at the surface of a solid body thereby increasing its active volume, (b) liquids associated with the solid body as a solid solution (non-polar and polar molecules), and (c) polar liquids reacting with solids to form a complex compound. The existence of these different kinds of swelling has been proved by X-ray spectrography (9).<sup>3</sup>

Although intramolecular swelling has been shown to take place in clays (4, 5, 9), the data in this study indicate that intermolecular or surface phenomena are responsible for most of the swelling. The results in tables 1, 3, 5, and 6 and in figure 1 show the effect of exchangeable cations on the swelling

<sup>3</sup> Most of the discussion in this paragraph has been based upon the work of Katz (9).

of three different aluminosilicates. It is obvious that the colloidal clays and bentonite differ considerably both in their capacities to swell and in their behavior to the different ions on the exchange complex. As previously pointed out in the case of clays, the K ion behaves similarly to the divalent cations

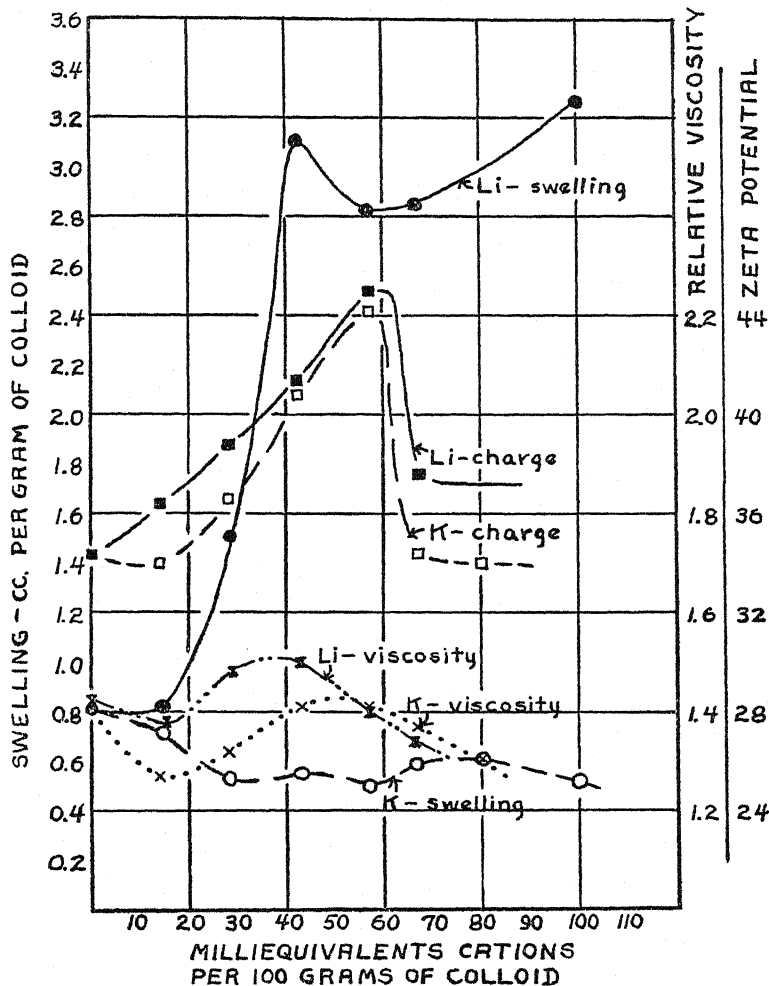


FIG. 1. COLLOIDAL PROPERTIES OF PUTNAM CLAY AS AFFECTED BY VARYING AMOUNTS OF EXCHANGEABLE Li AND K IONS

and the H ion in influencing the water sorption and swelling of these colloids. As a matter of fact, K-saturated clays swell less than any of the other clays. K-saturated bentonites, on the other hand, behave similarly to the Li- and Na-bentonites. These differences cannot be satisfactorily explained on the sole basis of ionic hydration.

A comparison of K- and Li-saturated Putnam colloids reveals several interesting facts concerning hydration. The data illustrated in figure 1 show the hydration of Putnam clay saturated with varying amounts of Li and K ions. Hydration is expressed in terms of relative viscosity and swelling. The zeta-potentials of the different systems are also shown. It is obvious that as the Li or K ions replace the exchangeable H ions on the surface of the colloidal particles the zeta-potential increases to a maximum at approximately the saturation capacity of the colloid. Hydration of the particles as measured by viscosity follows somewhat similar tendencies for both the Li- and K-clays. These particular relationships have been thoroughly discussed in a previous study (1). Swelling likewise increases with the concentration of Li ions on the exchange complex. The K ions, however, cause a significant decrease in the swelling of the clay. The data of Jenny (7) in table 8 show that the difference in the strength with which the Li and K ions are held on the surface in comparison with the H ion is not sufficient to explain such pronounced variations in the swelling. Likewise, the fact that Li- and K-saturated clays have about the same charge and dispersity does not add to the clarity of the problem. The differences cannot be interpreted directly in terms of the hydration of the two ions. Since the K- and Li-clays behave similarly with respect to hydration in an excess of water (colloidal suspension) it appears that the K-systems are unable to orient water around the surfaces of the primary colloidal particles whenever much energy is required for the dispersion of the secondary colloidal particles. The Li-colloid attracts water molecules very strongly even to the point of complete dispersion of aggregated systems. In colloidal suspension where the individual particles have been brought into suspension by some external force, the K-saturated surfaces do attract a rather large number of water molecules as evidenced by viscosity measurements.

Assuming that the amount of water oriented by the exchange complex is proportional to (a) the number of ions on the complex, (b) the tightness with which they are held, and (c) the field strength or orienting tendency of each ion as determined by its charge and size, the relative hydration of the different Putnam clays should be as follows: K = 1.0, Li = 2.3, Na = 1.4, Ca = 1.7, and Ba = 0.9. The relative swelling for each of these systems is 1, 10, 8, 1.8, and 1.7, respectively. These data strongly suggest that there are important influences contributing to the swelling of clays other than the effect of the exchangeable ions. It seems that the forces within the inner layer can attract to the colloidal surface water molecules as well as ions. Any explanation of the effect of the different ions on hydration must take into consideration not only the orienting tendency of the ions for water molecules, the number and kind of ions present<sup>4</sup> and their activities, but also the attractive power of the inner layer for water as it may be affected by ionic adsorption.

<sup>4</sup> After this paper was prepared, the attention of the authors was called to a forthcoming publication of Dr. E. W. Russell of the Rothamsted Experimental Station in which the effect of the exchangeable ions on hydration is thoroughly discussed.

The high swelling of bentonites in comparison with colloidal clays strongly suggests that the former attract large amounts of water as a result of forces

TABLE 9  
*Exchange of cations by different Putnam clay and bentonite systems [Jenny (7)]*  
Symmetry values

COLLOIDAL SYSTEM	NATURE OF CATION					
	Li	Na	K	Ca	Ba	H
<i>Adsorption</i>						
NH <sub>4</sub> -Putnam clay.....	29.9	35.3	51.3	63.6	71.7	84.9
H-Putnam clay.....	6.6	6.2	14.5	26.9	23.8	....
H-Bentonite.....	18.0	14.6	18.4	....	....	....
<i>Release</i>						
NH <sub>4</sub> Cl Putnam clays.....	57.0	58.9	42.0	29.3	....	6.9
NH <sub>4</sub> Cl Bentonites.....	46.5	49.6	43.7	....	....	14.5

TABLE 10  
*Effect of SiO<sub>2</sub>-sesquioxide ratio and exchange properties of colloidal clays on hydration*

COLLOIDAL PROPERTY	TYPE OF H-COLLOID							
	Bentonite	Luffkin clay	Wabash clay	Putnam	Susquehanna clay	Iredell clay	Davidson clay	Cecil clay
SiO <sub>2</sub> -R <sub>2</sub> O <sub>3</sub> ratio.....	5.0	3.8	3.2	3.2	2.3	1.78	1.44	1.3
Symmetry value (release by K)....	18.40	.....	.....	15.0	.....	16.66	20.33	.....
Exchange capacity, m.e./gm.....	0.95	0.82	0.78	0.65	0.47	0.35	0.12	0.13
Swelling, cc./gm.....	2.2	1.18	0.94	0.81	0.57	0.23	None	0.054
Heat of wetting, cal./gm.....	.....	15.0	13.9	13.8	11.7	.....	.....	5.9
Hygroscopicity (30 per cent H <sub>2</sub> SO <sub>4</sub> ) per cent by weight.....	21.5	20.1	.....	18.1	15.5	.....	.....	6.1
Swelling (cc.).....	.....	0.079	0.068	0.059	0.048	.....	.....	0.0091
Heat of wetting (cal.).....	.....	.....	.....	.....	.....	.....	.....	.....
Hygroscopicity (per cent).....	.....	1.34	.....	1.31	1.33	.....	.....	1.03
Heat of wetting (cal.).....	.....	.....	.....	.....	.....	.....	.....	.....
Swelling (cc.).....	2.44	1.44	1.20	1.24	1.21	0.66	.....	0.41
Exchange capacity (m.e.).....	.....	.....	.....	.....	.....	.....	.....	.....
Hygroscopicity (per cent).....	0.22	0.24	.....	0.28	0.33	.....	.....	0.47
Exchange capacity (m.e.).....	.....	.....	.....	.....	.....	.....	.....	.....
Swelling (cc.).....	10.23	5.87	.....	4.47	4.87	.....	.....	0.91
Hygroscopicity (cc.).....	.....	.....	.....	.....	.....	.....	.....	.....

associated with the inner layer of the colloidal surface. There are several experimental facts that indicate the presence of this type of hydration. If

a comparison is made of the swelling of the Li-, Na-, and K-saturated bentonites and clays it is seen that the bentonite systems swell 116, 175, and 1610 per cent more, respectively, than the corresponding clays. The relative number of effective ions per gram of colloid as calculated from the saturation capacities (table 10) and the symmetry values (table 9, release) are 0.44, 0.47, and 0.41 m.e. for the Li-, Na-, and K-saturated bentonites. For the corresponding Putnam clay systems these values are 0.37, 0.38, and 0.27 m.e. These data show that such large differences in swelling in the two systems cannot be explained on the basis of ionic hydration. Moreover, the K-saturated bentonite is similar to the Li- and Na-systems in its swelling. Base exchange studies (table 9) and viscosity and dispersion (table 4) measurements show the same similarities. Marshall's data on dispersion also point out that the different exchangeable cations including the divalent ion have similar effects on the dispersity of bentonite. He explains these differences on the basis that bentonite is a montmorillonitic type of aluminosilicate with a high hydration; Putnam clay is described as a beidellitic type of colloid. Inasmuch as the colloidal behavior of bentonite classifies it as being more hydrophilic in nature than Putnam clay, it seems plausible to interpret these differences in swelling and hydration to variations in the attractive forces of the inner layer and the resulting increased mobility of the adsorbed ions, causing a measurable osmotic type of swelling.

The data in table 10 obtained in this investigation and other studies on colloidal clays (1, 2, 10) are summarized to show the relation of swelling and hydration to the nature of colloid and its exchange properties. It is observed that swelling increases with the  $\text{SiO}_2$ -sesquioxide ratio and the exchange capacity of the colloid; hygroscopicity and heat of wetting also increase with these properties of the colloid. Although swelling, heat of wetting, and hygroscopicity increase with the exchange capacity of the colloid, the relationship is not a simple one, since the relative activities of the exchangeable ions and the colloidal surface must be considered in addition to the number of ions present. For example, bentonite swells 2.44 cc. per milliequivalent of exchangeable cations present; Lufkin clay swells 1.44 cc.; Wabash, Putnam, and Susquehanna clays swell about 1.20 cc.; and Iredell, Davidson, and Cecil colloids swell much less than 1 cc. per milliequivalent. On the other hand, the amount of water adsorbed by the colloid from an atmosphere of water vapor per milliequivalent of exchangeable ions present increases with decreasing exchange capacity. Perhaps the structure of the colloid exerts considerable influences on water adsorption from an atmosphere of water vapor. If the ratio of swelling to water adsorption (hygroscopicity) is compared, it is observed that bentonites swell considerably in excess of the adsorbed water. The amount of water used by the Cecil clay in the swelling process, however, is a trifle less than the adsorbed water. Apparently, only sufficient water is taken up by this lateritic type of clay to satisfy the adsorptive properties of the surface. The ratio of swelling to the energy of water adsorption is likewise very low with this colloid.



It has been previously suggested that the physical structure of the primary particles as well as their possible aggregates may play an important rôle in water sorption, especially when dried colloidal powders are permitted to react with relatively large amounts of water either as a result of contact with a free water surface (sorption experiments) or with an atmosphere of water vapor. In a system where the primary particles possess a porous structure the size of the pores naturally limits the amount of water that can be adsorbed on the internal surface. Since these pores may also contain capillary water, sorption experiments do not give a direct clue as to the affinity of this internal surface for water. Permutites are examples of porous aluminosilicates; colloids extracted from lateritic types of soil also suggest a somewhat porous constitution. These types of colloids do not swell in water even though they may adsorb varying amounts of water from an atmosphere of water vapor. Non-porous and non-aggregated soil colloids with plate-shaped particles, however, are able under these same conditions to saturate their affinity for water to the highest possible degree. Such seems to be true in the swelling of Li- and Na-saturated Putnam and Wabash colloids where the amount of swelling water attained the hydration values calculated from the viscosity data. An intermediary case between the swelling behavior of porous colloids and non-porous plate-shaped clays would be expected when the shape of the particles approaches that of a sphere.

Low sorption values will also be found in the case of porous aggregates (stable aggregation) especially if the affinity of the primary particle for water is appreciably lower than that for another soil particle. Such may be the case to a limited extent with K-, Ba-, Ca-, and H-colloids. A qualitative measure of these affinities is the ease of dispersion. If it is assumed, as the results of these investigations suggest, especially those with the H-clays with small amounts of organic matter, that the entire swelling is due to hydration, which in turn is proportional to the heat of wetting, then it can be concluded that Putnam, Wabash, and Lufkin clays have similarly shaped particles that are plate-like; Susquehanna and Cecil colloids seem to consist of either a more spherical type of particles or of porous primary particles.

It is obvious that the swelling or hydration of soil colloids is a rather complicated physical phenomenon. The results obtained in this investigation suggest certain interpretations of hydration in terms of the colloidal chemistry of the surface, that is, the effect of both the inner and outer parts of the electrical double layer in their relation to charge and hydration. It is interesting to compare these interpretations with the deductions of other investigators. Katz (8) has extensively studied the swelling of a large number of substances of widely varying character. Care was taken that swelling was not complicated by mechanical factors such as the porosity of the systems. From his experimental results Katz calculated, with the aid of thermodynamical reasoning, certain relationships between swelling pressure, heat of swelling, relative vapor pressure, etc. He compares the behavior of swelling substances to that of an ideal concentrated solution (Nernst), the heat of dilution of which can

be entirely changed into other forms of energy. Evidently the swelling of soils and clays is more complicated; but there is reason to believe that the hydration of clays follows the laws developed by Katz.

Terzaghi (13) has studied the swelling of elastic systems with porous structures (soils). He has interpreted the swelling of these systems as being due to the combined action of the surface tension of the water in the system and the elasticity of the solid components. Although the results of Terzaghi's work are of extreme importance in soil mechanics, a more physicochemical interpretation is necessary to describe the hydration phenomena in colloidal clay systems.

Mattson (12) has explained the swelling of colloidal clays on the basis of the Donnan equilibrium as developed by Wilson and by Proctor and Wilson. The data obtained in the present study indicate that the swelling of bentonites may be at least partially explained by the Donnan concept but that this type of swelling cannot account for an appreciable amount of the hydration displayed by the common clay colloids.

The work of Langmuir, Harkins, Debye, and others, who have developed the concept of molecular orientations on surfaces and interfaces and around ions, has been used in formulating the concept of swelling in the present investigation.

#### SUMMARY

A study has been made of the influence of the structure of soil colloids and of the amount and nature of ions at the surface on such colloidal properties as sorption of liquids, heat of wetting, viscosity of suspensions, zeta-potential of the dispersed particles, hygroscopicity, and hydration.

On the basis of these experimental data hydration is explained as being due in largest degree to the orienting influence on dipole molecules of the colloid surface as well as of the adsorbed cations. With special colloids (bentonite and alkali-saturated organic matter) an osmotic type of swelling seems to play a significant rôle.

The importance of the shape of the primary and secondary colloidal particles on the evaluation of swelling from sorption data is stressed.

The principal swelling theories are briefly discussed in their relation to the data and conclusions of this particlaur study.

#### REFERENCES

- (1) BAVER, L. D. 1929 The effect of the amount and nature of exchangeable cations on the structure of colloidal clay. *Missouri Agr. Exp. Sta. Res. Bul.* 129.
- (2) BAVER, L. D., AND HORNER, GLEN M. 1933 Water content of soil colloids as related to their chemical composition. *Soil Sci.* 36: 329-353.
- (3) DELUC 1791 *Phil. Trans.* 81: 1-42; 389-421, quoted by J. R. Katz (8), p. 49.
- (4) ENDELL, K., HOFMANN, U., AND WILM, D. 1933 Ueber die Natur der keramischen Tone. *Ber. Deut. Ker. Gesell.* 14: 407-438.
- (5) HOFMANN, V., ENDELL, K., AND WILM, D. 1933 Kristallstruktur und Quellung von Montmorillonit. *Ztschr. Kristallogr.* (A) 86: 340-348.

- (6) JANERT, H. 1934 Kationenaustausch und Wasseradsorption in Boeden. *Ztschr. Pflanzenernähr., Düngung, u. Bodenk.* 34 ( $H_2$ ): 100-108.
- (7) JENNY, HANS 1932 Studies on the mechanism of ionic exchange in colloidal aluminum silicates. *Jour. Phys. Chem.* 36: 2217-2258.
- (8) KATZ, J. R. 1917 Die Gesetze der Quellung. *Kolloidchem. Beihefte.* G: 1-182.
- (9) KATZ, J. R. 1933 The laws of swelling. *Trans. Faraday Soc.* 29: 279-300.
- (10) LUTZ, J. F. 1934 The physico-chemical properties of soils affecting soil erosion. *Missouri Agr. Exp. Sta. Res. Bul.* 212.
- (11) MARSHALL, C. E. 1931 Studies in the degree of dispersion of the clays. II. The influence of cations on the degree of dispersion. *Jour. Soc. Chem. Indus.* 50: 457-462.
- (12) MATTSON, SANTE 1932 The laws of soil colloidal behavior: VIII. Forms and functions of water. *Soil Sci.* 33: 301-322.
- (13) TERZAGHI, K. v. 1931 The swelling of two-phase systems. *Colloid Chemistry* (ed. J. Alexander) 3: 65-88.
- (14) WINTERKORN, HANS, AND BAVER, L. D. 1934 Sorption of liquids by soil colloids. I. Liquid intake and swelling by soil colloidal materials. *Soil Sci.* 38: 291-298.



## John Sharkey Carroll

1871-1935

John Sharkey Carroll, prominent in the fertilizer industry of this country for more than 30 years, died at his home in Jackson, Mississippi, on September 15.

Mr. Carroll was born in Oktibbeha County, Mississippi, in 1871. He received the bachelor of science degree, for work in agriculture, and the master of science degree, for work in agricultural chemistry, from the Mississippi Agricultural College. For more than 10 years he served that institution as instructor and, later, as assistant professor of chemistry and assistant state chemist. From 1904 until his death, he was connected with the agricultural and scientific work of the potash interests.

Mr. Carroll was a member of several learned societies, agricultural associations, and local organizations.





## THE RELATION OF SOIL TREATMENT TO THE NODULATION OF PEANUTS<sup>1</sup>

H. B. MANN<sup>2</sup>

*North Carolina Agricultural Experiment Station*

Received for publication March 15, 1935

The use of calcium carbonate and calcium sulfate in the production of large type peanuts has become an almost universal practice. Little attention has been given, however, to the effects of these salts except that upon the final yield of nuts. Under some conditions on application of either or both of these materials may mean the difference between crop failure and success, whereas under other conditions they are of no apparent value. What these conditions are has not been determined. A part of the investigations designed to study this problem has shown certain relationship between nodulation and soil treatments.

### HISTORICAL REVIEW

Previous work along this line with peanuts has been limited. Duggar (5) working with Spanish peanuts reported decreased nodulation during the first 6 weeks resulting from separate applications of superphosphate, basic phosphate, and hydrated lime in immediate contact with the seed. Increased nodulation was noted from applications of 200 pounds per acre of sulfur. Neither the type of soil used in these investigations nor its reaction was reported.

Although a vast amount of work has been done with legumes in general, there is no agreement among investigators as to the effect of various inorganic salts on nodulation. It would appear from the work of Pitz (13), Reimer and Tartar (15), and Neller (9) that calcium sulfate and sulfur exert a stimulating effect on the nodulation of legumes. Wilson (17), however, found that not only calcium sulfate but sulfates in general had a depressing effect upon the nodulation of soybeans. Carbonates appeared to have a stimulating effect, most of which he attributed to the influence of the alkaline radical with which the carbonates were combined.

Supported by many early investigations, and the comparatively recent ones of Prucha (14), Fellers, (6) Wilson (17), Albrecht and Davis (2, 3), and Scanlan (16), calcium carbonate is usually considered as having a stimulating effect upon nodulation. However, Perkins (10, 11) was unable to get increased nodulation

<sup>1</sup> Published with the approval of the director of the North Carolina Experiment Station as paper 82 of the Journal Series.

<sup>2</sup> Agronomist in soil fertility of the North Carolina Agricultural Experiment Station.

of soybeans from the use of either calcium or potassium compounds. Harmful effects from large applications of calcium oxide or calcium carbonate have been reported by several German investigators, the more recent of whom are Pfeiffer and Simmermacher (12), Merckenschlager (8), and Boas and Merckenschlager (4).

These conflicting results serve to illustrate the necessity of further investigations along these lines as well as to indicate the importance of such factors as growth period, soil type, previous soil treatment, and amount of chemicals applied. This investigation was undertaken to give further information regarding the effect of the latter factors upon nodulation of peanuts.

#### EXPERIMENTAL METHODS

Glazed pots of  $2\frac{1}{2}$  gallon capacity, filled with a definite amount of soil for each type used, were uniformly inoculated with a commercial peanut culture and maintained as nearly as possible at a constant optimum moisture content. Seven Virginia Bunch peanut seeds were planted in each pot and after germination were thinned to five plants. Those were grown in the greenhouse, and at various stages of growth the soil was washed from the roots of the plants and nodulation records were made. Soil samples were taken for pH determinations, which were made by the quinhydrone method, and dry weights of plants recorded. All results reported are the average of duplicate treatments.

#### NODULATION AND GROWTH OF PEANUTS AND THE pH OF SOILS AS INFLUENCED BY CALCIUM CARBONATE, CALCIUM SULFATE, AND SULFUR

There are two general types of soil on which large peanuts are usually grown. Norfolk sandy loam, which is light in color, well drained, sandy, and low in organic matter, represents one of these. The other type as represented by the Coxville fine sandy loam is dark in color, less well drained, finer in texture, and higher in organic matter. Experiments were made with these two types of soil to determine the effects of applications of calcium carbonate, calcium sulfate, and sulfur upon nodulation and growth of peanuts and the reaction of the soil.

##### *Virgin Norfolk sandy loam soil*

On February 24, 1932, 48 pots were set up with virgin Norfolk sandy loam soil (pH 5.3) as outlined under experimental methods. These were divided into eight series of six treatments each, the latter as follows: (a) 2,000 pounds of calcium carbonate per acre; (b) 2,000 pounds calcium sulfate; (c) 400 pounds of ground sulfur; (d) 400 pounds of ground sulfur and 2,000 pounds of calcium carbonate; (e) 2,000 pounds of calcium sulfate and 2,000 pounds of calcium carbonate; (f) left untreated for check. The materials were thoroughly mixed with the entire amount of soil in each pot.

The number of nodules per pot of five plants, the dry weights of plants, and the pH of soils were determined on duplicate series on March 14, March 30, April 11, and August 24, 1932. When the last records were made on August 24



the peanuts had reached the stage of maturity at which commercial nuts are dug. Treatments and results are shown in table 1.

Eighteen days after planting, when the first series of plants were harvested, no nodules had developed sufficiently on any of the roots to be identified. At all other stages of growth as compared with the checks calcium carbonate increased nodulation. This increase became greater as the plants developed. Calcium sulfate both retarded and reduced nodulation. No nodules were found in the calcium sulfate pots until the third series was harvested 48 days after planting. Four hundred pounds of sulfur per acre prevented nodulation at all stages of growth, whereas the combination of sulfur and calcium carbonate produced about the same number of nodules as the checks. The combined application of calcium sulfate and calcium carbonate had very little

TABLE 1

*Nodulation and growth of peanuts and the pH of virgin Norfolk sandy loam soil as influenced by calcium carbonate, calcium sulfate, and sulfur*

Original pH 5.3. Planted February 24, 1932

TREATMENT PER ACRE	AVERAGE NUMBER OF NODULES PER POT (5 PLANTS)				AVERAGE DRY WEIGHT OF PLANTS PER POT (5 PLANTS)				pH OF SOIL			
	Days after planting											
	18	34	48	180	18	34	48	180	18	34	48	180
					gm.	gm.	gm.	gm.				
None.....	0	12	160	405	3.5	5.8	10.2	27.4	5.25	5.40	5.40	5.10
2,000 lbs. CaCO <sub>3</sub> .....	0	13	215	1,090	2.3	4.6	10.9	36.5	6.50	6.75	6.70	5.60
2,000 lbs. CaSO <sub>4</sub> .....	0	0	50	175	2.7	3.2	9.0	21.0	4.75	4.60	4.90	5.00
400 lbs. sulfur.....	0	0	0	0	1.9	4.6	6.4	20.9	3.80	3.80	3.90	4.10
400 lbs. sulfur; 2,000 lbs. CaCO <sub>3</sub> .....	0	5	200	395	2.7	5.9	11.3	36.0	4.90	4.85	4.70	5.00
2,000 lbs. CaSO <sub>4</sub> ; 2,000 lbs. CaCO <sub>3</sub> .....	0	6	155	725	1.5	2.8	8.8	30.2	4.95	5.90	5.80	5.55

effect upon nodulation until the last series was harvested, when a decided increase was found.

No severe depression in growth was noted from any of the treatments. However, as shown by the dry weights, calcium carbonate stimulated growth, whereas calcium sulfate and sulfur retarded it. In general, this is the same influence exerted by these materials upon nodulation, but their effects upon growth were by no means so marked. The growth of plants could not be taken as a measure of nodulation.

There was an inverse relation between the acidity of the soil and nodulation. The treatments that increased acidity decreased nodulation and those that decreased acidity increased nodulation. The fact that calcium sulfate increased the acidity of the soil at all stages of growth probably accounts for the retardation and reduction of nodulation from its use. This conclusion is

supported by Albrecht (1), who recently reported that nodulation of soybeans failed on soils as acid as pH 5.0 even in the presence of sufficient calcium. The failure of nodulation in the sulfur-treated pots was also undoubtedly due to the high degree of soil acidity produced by the treatment.

*Virgin Coxville fine sandy loam*

The preceding experiment was repeated on July 13, 1933 with virgin Coxville fine sandy loam (pH 4.5). Treatments and results are shown in table 2.

In this experiment the first series was not torn down until 28 days after planting, at which time nodules had developed in all pots except those treated with single applications of calcium sulfate and sulfur. The nodulation data agree very closely with those obtained on the Norfolk soil. Calcium carbon-

TABLE 2

*Nodulation and growth of peanuts and the pH of virgin Coxville fine sandy loam soil as influenced by calcium carbonate, calcium sulfate, and sulfur*

Original pH 4.5. Planted July 13, 1933

TREATMENT PER ACRE	AVERAGE NUMBER OF NODULES PER POT (5 PLANTS)				AVERAGE DRY WEIGHT OF PLANTS PER POT (5 PLANTS)				pH OF SOIL			
	Days after planting											
	28	36	48	173	28	36	48	173	28	36	48	173
					gm.	gm.	gm.	gm.				
None.....	15	17	34	177	5.0	6.1	12.0	30.9	5.00	5.00	5.00	4.45
2,000 lbs. CaCO <sub>3</sub> .....	93	156	154	228	6.6	8.9	16.7	29.5	5.80	5.50	5.35	4.85
2,000 lbs. CaSO <sub>4</sub> .....	0	0	10	156	6.2	9.0	17.0	31.2	4.40	4.25	4.30	4.30
400 lbs. sulfur.....	0	0	0	0	5.1	6.5	13.3	30.0	3.85	3.75	4.20	4.20
400 lbs. sulfur; 2,000 lbs. CaCO <sub>3</sub> .....	5	15	24	182	5.3	7.8	15.1	30.3	4.25	4.15	4.25	4.45
2,000 lbs. CaSO <sub>4</sub> ; 2,000 lbs. CaCO <sub>3</sub> .....	25	37	62	216	6.0	11.5	18.6	29.3	4.80	4.65	4.90	4.45

ate stimulated and increased, calcium sulfate retarded and reduced, and sulfur prevented nodulation.

The dry weights of the plants gave no indication of the degree of nodulation at any stage of growth. At maturity all of the treatments had produced approximately the same amount of growth. The reaction of the Coxville soil was not influenced so much by the various treatments as was that of the Norfolk, undoubtedly because of the higher organic matter content and consequent greater buffer capacity of this soil. The general effect of the treatments on soil reaction was, however, the same on both soils. Calcium carbonate reduced, calcium sulfate slightly increased, and sulfur greatly increased acidity.

*Cultivated and limed Norfolk sandy loam soil*

It is evident that under the conditions of the two preceding experiments with virgin Norfolk (pH 5.3) and virgin Coxville (pH 4.5) soils, calcium car-

bonate stimulates, calcium sulfate retards and reduces, and sulfur prevents peanut nodulation. Practically all large type commercial peanuts, however, are grown on soils that have been previously limed and cultivated. For this reason a third experiment was made using a Norfolk sandy loam soil which had been in cultivation, with peanuts in rotation, for at least 50 years. When the experiment was set up August 24, 1932, the pH of the soil was 6.6, indicating that it had been limed. The results of this experiment are given in table 3.

Contrary to the results obtained with the two previous highly acid soils, calcium carbonate did not increase nodulation. At the last two counts the check pots had slightly more nodules than did those treated with calcium carbonate. As was the case with the other soils, calcium sulfate retarded and reduced nodulation, but its effect was not so marked. Even though this soil

TABLE 3

*Nodulation and growth of peanuts and the pH of cultivated Norfolk sandy loam soil as influenced by calcium carbonate, calcium sulfate, and sulfur*

Original pH 6.6. Planted September 24, 1932

TREATMENT PER ACRE	AVERAGE NUMBER OF NODULES PER POT (5 PLANTS)				AVERAGE DRY WEIGHT OF PLANTS PER POT (5 PLANTS)				pH OF SOIL			
	Days after planting											
	22	46	69	154	22	46	69	154	22	46	69	154
					gm.	gm.	gm.	gm.				
None.....	0	34	150	395	3.4	7.7	12.3	26.3	6.25	6.25	6.30	5.80
2,000 lbs. CaCO <sub>3</sub> .....	0	36	142	377	3.9	7.1	12.8	28.0	7.20	7.40	7.30	6.50
2,000 lbs. CaSO <sub>4</sub> .....	0	5	79	320	3.7	8.5	12.1	26.0	5.45	5.70	5.80	5.75
400 lbs. sulfur.....	0	0	0	0	3.5	6.2	12.1	24.8	4.50	4.00	4.75	5.10
400 lbs. sulfur; 2,000 lbs. CaCO <sub>3</sub> .....	0	35	104	404	3.3	6.3	11.4	26.5	5.30	5.00	5.50	6.10
2,000 lbs. CaSO <sub>4</sub> ; 2,000 lbs. CaCO <sub>3</sub> .....	0	33	114	414	4.0	6.9	12.5	23.8	6.90	7.20	7.15	6.30

had been limed to pH 6.6, 400 pounds of sulfur prevented nodulation of the peanuts at all stages of growth. These effects of sulfur upon nodulation are contrary to those reported by Duggar (5), who obtained increased nodulation from 200-pound applications. Further experiments should be made to determine the effect of varying amounts of sulfur on different soil types.

As in the other two experiments, there was no definite correlation between plant growth and nodulation. These results are further supported by field observations on various soil types. Examination of the plants in a large number of fields where the growth was poor showed the peanuts in many of them to be poorly nodulated, in others they were well nodulated, and in a very few fields there was excessive nodulation. An example of this latter condition is illustrated in plate 1, which shows excessive nodulation on the roots of inferior plants growing on a Portsmouth fine sandy loam (pH 5.5). The better

plants growing in the same field were not so heavily nodulated. The heavy nodulation, associated with weakened plants, may indicate that excessive nodulation is indicative of a disease-producing phenomena on the plant. A failure of Austrian winter peas apparently due to nodule bacteria has been reported by Leonard (8).

#### NODULATION AND GROWTH OF PEANUTS AND THE pH OF SOILS AS INFLUENCED BY CALCIUM CARBONATE

The fact that increased nodulation was obtained from applications of calcium carbonate on both the virgin Norfolk and virgin Coxville soils and that no increase was obtained on the limed Norfolk soils, indicates the importance of the amount of calcium carbonate and suggests a possible explanation for the conflicting results regarding the effect of calcium carbonate on the nodulation of legumes. The following experiment was made to study the effect of varying amounts of calcium carbonate upon the nodulation of peanuts.

##### *Virgin Norfolk sandy loam soil*

Eight series of seven pots each were set up, as in previous experiments, on July 12, 1934, with virgin Norfolk sandy loam soil (pH 5.0). One pot of each series was treated with the following amounts of calcium carbonate per acre: 2,000, 4,000, 6,000, 8,000, 12,000, and 16,000 pounds. The seventh pot was left untreated as a check. In table 4 are shown the results obtained at the four periods of growth.

Moderate applications of calcium carbonate increased nodulation, whereas heavy applications both retarded and reduced it. The reduction of nodulation was greatest with the heaviest applications of calcium carbonate. Although the nodulation curves are not identical, they exhibit the same trends at the four stages of growth, showing a maximum nodulation from moderate applications of calcium carbonate.

As pointed out by Jones and Tisdale (7), nodule count alone may not always be a true measure of the amount of nodulation. Photographs of the actual nodules from each treatment at the first and last counts are shown in plate 2.

No chlorosis or severe injury to growth developed from any of the treatments. There was a stimulation of growth from moderate applications of calcium carbonate which the very heavy applications reduced. The effect of the various treatments upon growth was not so marked as upon nodulation.

At all sampling periods, increasing amounts of calcium carbonate were attended by decreasing acidity or increasing alkalinity. Nodulation was very poor on all soils limed to pH 7.5 or above.

##### *Virgin Coxville fine sandy loam soil*

To determine whether or not heavy applications of calcium carbonate would also reduce nodulation of peanuts on a well-buffered soil high in organic

matter, the preceding experiment was repeated with virgin Coxville fine sandy loam soil (pH 4.5). The treatments and results are shown in table 5.

As was the case with the Norfolk soil, medium applications of calcium carbonate stimulated nodulation whereas heavy applications reduced it. The

TABLE 4

*Nodulation and growth of peanuts and the pH of virgin Norfolk sandy loam soil as influenced by calcium carbonate*

Original pH 5.0. Planted July 12, 1934

CaCO <sub>3</sub> APPLIED PER ACRE	AVERAGE NUMBER OF NODULES PER POT (5 PLANTS)				AVERAGE DRY WEIGHT OF PLANTS PER POT (5 PLANTS)				pH OF SOIL			
	Days after planting											
	35	57	94	146	35	57	94	146	35	57	94	146
<i>pounds</i>					<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>				
None	30	33	61	73	10.3	15.9	21.0	26.4	5.05	5.10	5.20	5.20
2,000	39	57	62	117	14.9	21.2	24.6	29.1	5.90	5.85	5.75	5.55
4,000	19	40	76	67	17.8	19.3	24.9	28.5	6.75	6.65	6.40	6.10
6,000	9	22	80	86	14.5	19.5	25.8	30.0	7.40	7.50	7.15	7.15
8,000	8	15	24	26	13.3	18.8	23.7	26.7	7.70	7.90	7.45	7.60
12,000	0	5	26	36	10.3	15.5	22.3	24.4	7.80	8.00	7.65	8.00
16,000	0	3	2	12	11.2	14.4	16.3	21.1	7.90	8.15	7.75	8.05

TABLE 5

*Nodulation and growth of peanuts and the pH of virgin Coxville fine sandy loam soil as influenced by calcium carbonate*

Original pH 4.5. Planted August 8, 1934

CaCO <sub>3</sub> APPLIED PER ACRE	AVERAGE NUMBER OF NODULES PER POT (5 PLANTS)				AVERAGE DRY WEIGHT OF PLANT PER POT (5 PLANTS)				pH OF SOIL			
	Days after planting											
	31	63	91	115	31	63	91	115	31	63	91	115
	<i>pounds</i>				<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>				
None	61	182	150	166	8.9	10.8	16.2	21.3	5.00	5.05	4.90	4.80
2,000	157	611	1,596	1,717	11.8	15.2	20.6	30.0	5.80	5.50	5.30	5.20
4,000	224	939	1,192	1,961	13.0	16.0	22.3	33.3	5.95	5.80	5.60	5.55
6,000	260	1,039	1,294	1,461	12.3	17.0	22.9	32.9	6.40	6.05	6.00	6.00
8,000	174	607	409	1,185	12.8	18.2	21.8	33.1	6.65	6.35	6.25	6.35
12,000	12	84	26	62	13.3	15.0	22.0	33.2	7.60	7.50	7.15	7.10
16,000	6	10	17	19	12.0	14.1	21.0	26.1	7.95	7.90	7.55	7.40

nodulation curves are in general very similar to those obtained on the Norfolk soil except that a much larger number of nodules was produced. Photographs of the actual nodules produced with each treatment at the first and last counts are shown in plate 3.

The use of calcium carbonate even at the excessive rate of 16,000 pounds per

acre improved the color and increased the dry weight of the plants over the checks. The greatest growth was produced by applications ranging from 4,000 to 12,000 pounds per acre. The pH of the Coxville soil was not increased so much by heavy application of calcium carbonate as was that of the Norfolk. As was the case with the Norfolk soil, however, applications above 6,000 pounds per acre materially reduced nodulation even though the pH was only slightly above 6.

The results offer an explanation for the conflicting reports as to the effect of calcium carbonate upon the nodulation of legumes. In these experiments calcium carbonate both increased and decreased peanut nodulation, the response depending upon the amount of calcium carbonate applied and that already present in the soil. Moderate amounts of calcium carbonate on unlimed soils increased, but similar applications on heavily limed soils and heavy applications on unlimed soils decreased, nodulation.

#### SUMMARY

Calcium carbonate applied at the rate of 2,000 pounds per acre to virgin Norfolk sandy loam (pH 5.3) and to virgin Coxville fine sandy loam (pH 4.5) increased nodulation of peanuts throughout the growing season. Similar applications to a cultivated Norfolk sandy loam that had been previously limed to pH 6.6 did not increase nodulation. On this soil during the latter part of the growing season there was a slight reduction of peanut nodulation from the use of calcium carbonate.

Calcium sulfate broadcast at the rate of 2,000 pounds per acre both delayed and reduced nodulation in all three soils.

Probably because of the high acidity produced, sulfur applied to the aforementioned soils, at the rate of 400 pounds per acre, prevented nodulation of peanuts at all stages of growth.

Combined applications of sulfur and calcium carbonate or calcium sulfate and calcium carbonate had little effect upon the nodulation of peanuts, except that at maturity the combination of calcium sulfate and calcium carbonate usually increased nodulation.

The growth of peanut plants, as measured by dry weight, could not be directly correlated with nodulation.

Calcium carbonate decreased, calcium sulfate slightly increased, and sulfur greatly increased, acidity of all the soils used. Probably because of its greater buffer capacity, the Coxville soil resisted reaction changes to a greater extent than either of the Norfolk soils.

Varying applications of calcium carbonate to virgin Norfolk and Coxville soils had quite different effects upon peanut nodulation. Many more nodules were produced on the Coxville than on the Norfolk soil, but the response to liming was similar on both. Moderate amounts of calcium carbonate stimulated and increased nodulation, but heavy applications retarded and reduced it.

These results offer an explanation for the conflicting reports as to the effect of lime upon legume nodulation.

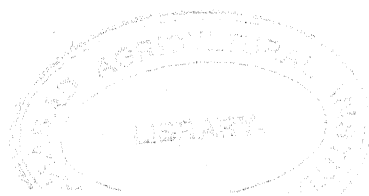
## REFERENCES

- (1) ALBRECHT, WM. A. 1933 Inoculation of legumes as related to soil acidity. *Jour. Amer. Soc. Agron.* 25: 512-522.
- (2) ALBRECHT, W. A., AND DAVIS, F. L. 1929 Physiological importance of calcium in legume inoculation. *Bot. Gaz.* 88: 310-321.
- (3) ALBRECHT, W. A., AND DAVIS, F. L. 1929 Relation of calcium to the nodulation of soybeans on acid and neutral soils. *Soil Sci.* 28: 261-279.
- (4) BOAS, F., AND MERKENSCHLAGER, F. 1923 Die Lupine als Objekt der Pflanzenforschung. Paul Parey, Berlin.
- (5) DUGGAR, J. F. 1931 Effects of sulphur and phosphates on nodule numbers. *Forty-second Ann. Rpt. Agr. Exp. Sta. Ala. Polytech. Inst.* 1931: 54.
- (6) FELLERS, C. R. 1918 The effect of inoculation, fertilizer treatment and certain minerals on the yield, composition and nodule formation of soybeans. *Soil Sci.* 6: 81-129.
- (7) JONES, F. R., AND TISDALE, W. B. 1921 Effect of soil temperature upon the development of nodules on the roots of certain legumes. *Jour. Agr. Res.* 12: 17-31.
- (8) LEONARD, LEWIS T. 1930 A failure of Austrian winter peas apparently due to nodule bacteria. *Jour. Amer. Soc. Agron.* 22: 277-279.
- (9) MERKENSCHLAGER, F. 1921 Die Chlorose der Lupine auf Kalkboden. *Führung's Landw. Ztg.* 70: 19-24.
- (10) NELLER, J. R. 1926 Effect of sulphur upon nitrogen content of legumes. *Indus. and Engin. Chem.* 18: 72-73.
- (11) PERKINS, A. T. 1924 The effect of several mineral fertilizers upon the nodulation of Virginia soybeans. *Soil Sci.* 17: 439-447.
- (12) PERKINS, A. T. 1924 A note on the nodulation of soybeans. *Soil Sci.* 17: 449-456.
- (13) PFEIFFER, T., UND SIMMERMACHER, W. 1919 Die Kalkfeindlichkeit der Lupine. *Landw. Vers. Sta.* 93: 1-47.
- (14) PITZ, W. 1916 Effect of elemental sulfur and of calcium sulfate on certain of the higher and lower forms of plant life. *Jour. Agr. Res.* 5: 771-780.
- (15) PRUCHA, M. J. 1915 Physiological studies of *Bacillus radicolica* of Canada field pea. *N. Y. (Cornell) Agr. Col. Mem.* 5: 1-83.
- (16) REIMER, F. C., AND TARTAR, H. V. 1919 Sulfur as a fertilizer for alfalfa in southern Oregon. *Ore. Agr. Exp. Sta. Bul.* 163.
- (17) SCANLAN, R. W. 1928 Calcium as a factor in soybean inoculation. *Soil Sci.* 25: 313-325.
- (18) WILSON, J. K. 1917 Physiological studies of the *Bacillus radicolica* of the soybean (Soja Max Piper) and of the factors influencing nodule production. *N. Y. (Cornell) Agr. Exp. Sta. Bul.* 386: 369-413.

## PLATE 1

EXCESSIVE NODULATION ON THE ROOTS OF INFERIOR PEANUTS GROWN ON  
PORTSMOUTH FINE SANDY LOAM (pH 5.5)





## PLATE 2

NODULATION OF PEANUTS IN VIRGIN NORFOLK SANDY LOAM (pH 5.0) AS AFFECTED  
BY APPLICATIONS OF CALCIUM CARBONATE

FIG. 1. Nodules per pot of five plants 35 days after planting. *A*, no calcium carbonate; *B*, 2,000; *C*, 4,000; *D*, 6,000; *E*, 8,000; *F*, 12,000; and *G*, 16,000 pounds calcium carbonate per acre.

FIG. 2. Nodules per pot of five plants at maturity, 146 days after planting. *A*, no calcium carbonate; *B*, 2,000; *C*, 4,000; *D*, 6,000; *E*, 8,000; *F*, 12,000; and *G*, 16,000 pounds calcium carbonate per acre.

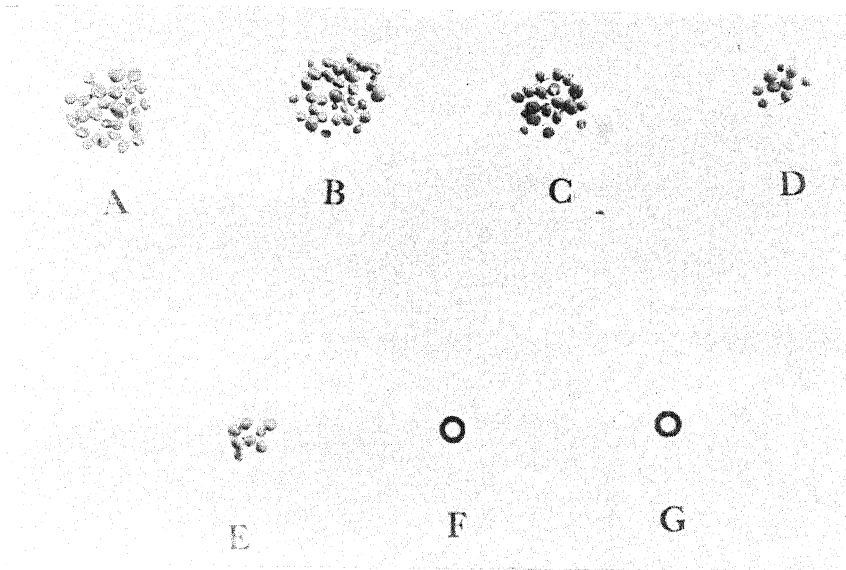


FIG. 1

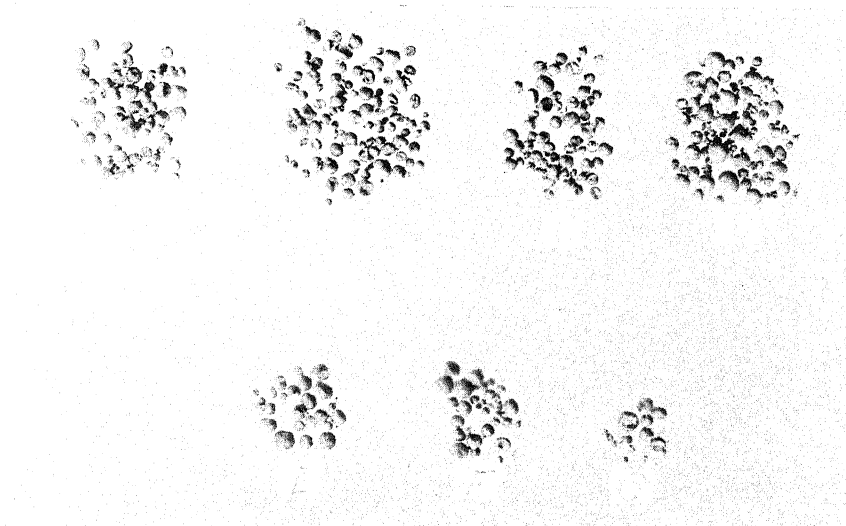


FIG. 2

PLATE 3

NODULATION OF PEANUTS IN VIRGIN COXVILLE FINE SANDY LOAM (pH 4.5) AS  
AFFECTED BY APPLICATIONS OF CALCIUM CARBONATE

FIG. 1. Nodules per pot of five plants 31 days after planting. *A*, no calcium carbonate; *B*, 2,000; *C*, 4,000; *D*, 6,000; *E*, 8,000; *F*, 12,000; and *G*, 16,000 pounds calcium carbonate per acre.

FIG. 2. Nodules per pot of five plants at maturity, 115 days after planting. *A*, no calcium carbonate; *B*, 2,000; *C*, 4,000; *D*, 6,000; *E*, 8,000; *F*, 12,000; and *G*, 16,000 pounds calcium carbonate per acre.

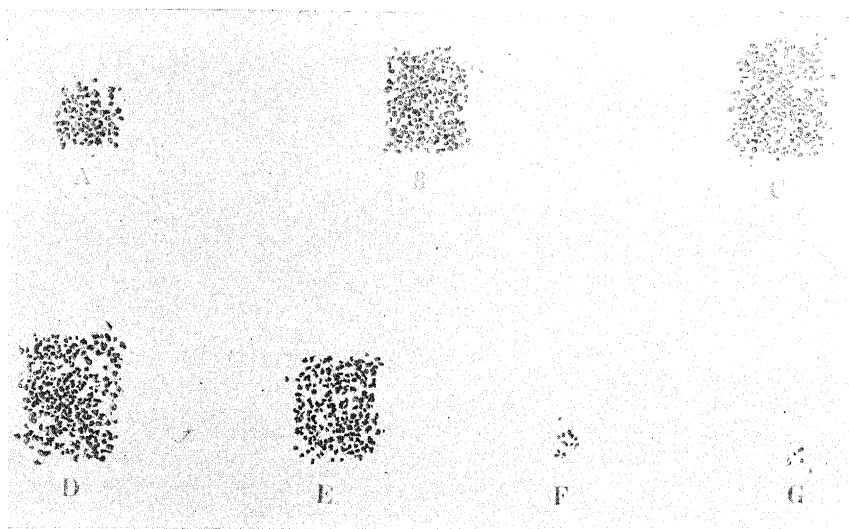


FIG. 1

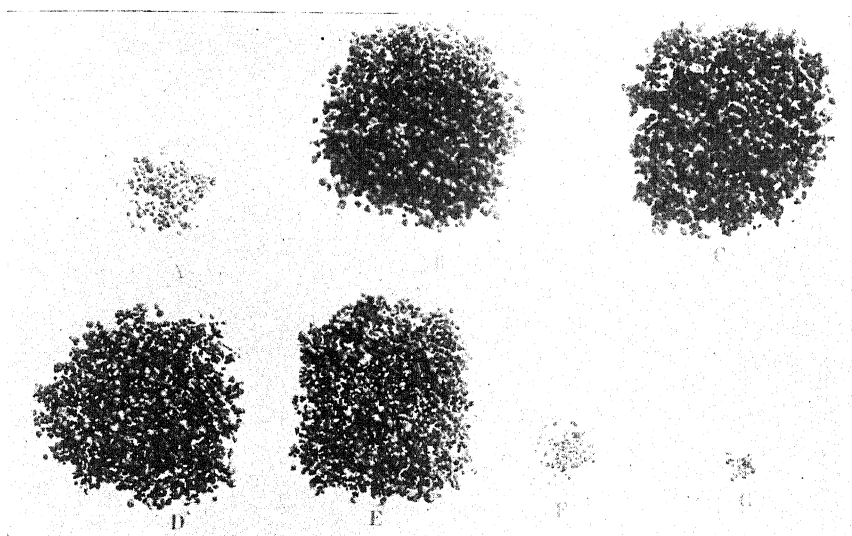



FIG. 2





## THE RELATION OF SOIL EROSION TO CERTAIN INHERENT SOIL PROPERTIES<sup>1</sup>

J. F. LUTZ<sup>2</sup>

*North Carolina State College*

Received for publication April 5, 1935

It has been observed that some soils erode easily whereas others under the same conditions of rainfall, vegetation, and topography erode very little, apparently because of differences in their physical or chemical properties. Some very valuable data on erosion control with different systems of management have been obtained (4, 13, 25), but our knowledge of the physical and chemical properties of soils which influence erosion has not been materially increased by these field experiments.

It is the object of this paper to present the results of a laboratory study of the physical and chemical properties of several soils that are known to vary in their erosiveness, and to show that certain of these properties play an important rôle in determining the susceptibility of a soil to erosion.

### PROPERTIES OF THE SOIL INFLUENCING EROSION

The amount of erosion depends partly upon the amount and the velocity of run-off water and partly upon soil properties. The amount of run-off from any given rain depends upon the rate of water absorption and the permeability of the soil. The permeability of a soil profile is determined by the rate of percolation through the least permeable layer, which in most upland soils is the B horizon. Janota (14) found that soils with a total pore volume of less than 40 per cent were impermeable. Bayer (6) observed that a soil with 5.9 per cent of air pores at a depth of 16 to 20 inches was well drained, but one with an air capacity of 2 per cent at the same depth was rather poorly drained. Slater and Byers (26) found that the rate of percolation of water through a number of soil cores was correlated with the silt content of the soil. Antipov-Karatajev (3) reported that the rate of filtration was a function of the colloid content of the soil and that the filtration velocity through soils depended upon the nature of the exchangeable ions present. The rate of filtration followed the series:  $\text{Fe} > \text{Ca} > \text{Mg} > \text{NH}_4 > \text{Na}$ .

Middleton (23) found that the best indexes to erosiveness were the dispersion ratio, the ratio of colloid content to moisture equivalent, the erosion ratio,

<sup>1</sup> A part of a thesis presented to the Graduate School of the University of Missouri in partial fulfillment of the requirements for the degree of doctor of philosophy.

<sup>2</sup> Assistant professor of soils, North Carolina State College. The author is indebted to Dr. L. D. Bayer for his many helpful suggestions during this investigation.

and the silica-sesquioxide ratio. Soils with a low silica-sesquioxide ratio were difficult to disperse.

Soils differ in the amount of material eroded per unit of run-off water. Carefully controlled experiments (25) have shown that the amount of erosion per cubic foot of run-off decreased from 0.881 pound to 0.477 pound as a result of plowing under organic matter. Baver and Rhoades (8) have shown that soils high in organic matter contain from 15 to 30 per cent more granules than those low in organic matter and that the granules are three times more stable when shaken with water for 100 minutes. Jenny (16) found that cultivation for 40 years, as compared with a virgin prairie, caused a 38 per cent decrease in organic matter and a 28 per cent decrease in sand-size granules. Burr and Russel (12) report that the addition of organic matter increased the porosity of the soil and the stability of the granules. Data given by Middleton et al. (24) indicate an inverse relation between the organic matter content and the erosion and dispersion ratios.

#### *Mechanical and aggregate analyses*

The Iredell sandy clay loam and the Davidson clay were selected for studying the physical properties of soils influencing erosion, because field observations have shown that the Iredell is an erosive soil and the Davidson a comparatively non-erosive one. There is a higher percentage of clay in all horizons of the Davidson than in the corresponding horizons of the Iredell (19). This is especially true in the A horizon. This horizon of the Iredell contains more than twice as much sand and 1.5 times more sand plus silt than the same horizon of the Davidson. Such a difference in texture might suggest that the Iredell was less erosive than the Davidson, especially since the B horizon of the Davidson contains more clay than the B layer of the Iredell. There is, however, a marked difference in the physical condition of the clay. The Iredell B horizon is a brownish yellow, heavy, plastic, sticky, and impervious clay when wet, which shrinks, cracks, and becomes very hard when dry. The Davidson, on the other hand, is a dark red, heavy but friable clay which breaks into large lumps that are easily crumbled into small fragments or granules.

The difference in the character of the B horizon of these two soils is shown by the extent to which they are aggregated. Granulation was measured by the Kopecky type of elutriator (8). The soils were dried just enough so they could be gently rubbed through a 2-mm. sieve, and were then placed in the elutriator without further treatment. In order to obtain ultimate dispersion they were shaken over night in a reciprocal shaker after treatment with a dispersing agent. The Iredell soil was dispersed with  $\text{Na}_2\text{C}_2\text{O}_4$ . The Davidson, however, flocculated in the presence of  $\text{Na}_2\text{C}_2\text{O}_4$ ; consequently,  $\text{NaOH}$  was used as the peptizing agent. Although  $\text{NaOH}$  effectively dispersed the natural Davidson soil, the electrodyalyzed colloid was not dispersed by any concentration of base. Apparently, the small amount of  $\text{Cl}$  ions in the natural soil aided in obtaining dispersion. A considerable quantity of  $\text{Cl}$  ions was found in the anode chamber during electrodialysis.



A careful analysis of figures 1 and 2 shows several very important facts concerning the extent and character of aggregation of the A and B horizons of the profiles. If the total percentage of aggregates in the soil, as represented by the cross-hatched portion of the graphs, is considered, it is noted that both

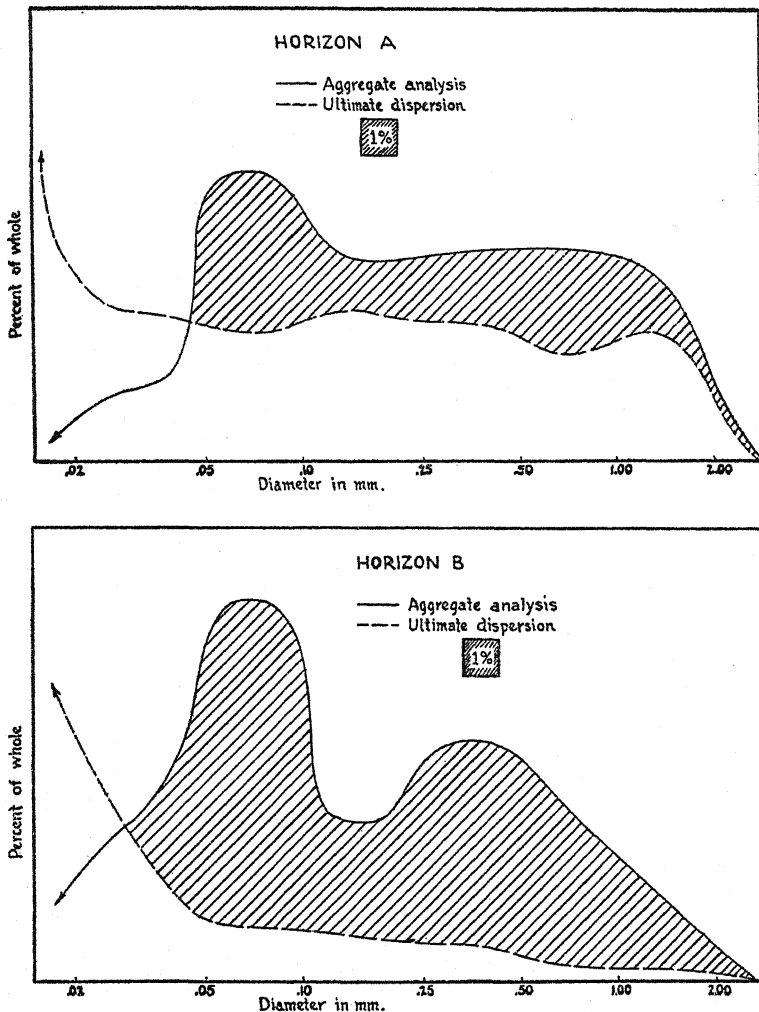


FIG. 1. SIZE-FREQUENCY DISTRIBUTION CURVE OF IREDELE SANDY CLAY LOAM WITH AND WITHOUT DISPERSION

soils are rather highly granulated. Since the curves for ultimate dispersion and aggregate analysis cross at about 0.05 mm., this value was chosen as the lower limit of aggregate size in calculating the total degree of aggregation.

The graphs show that the Davidson contains 15 to 20 per cent more aggre-

gates in each horizon than the Iredell. Nevertheless, there is a relatively high content of total aggregates in the Iredell. The B horizon<sup>3</sup> contains 64 per cent of granules, which is only 9 per cent less than the Davidson. In the Davidson

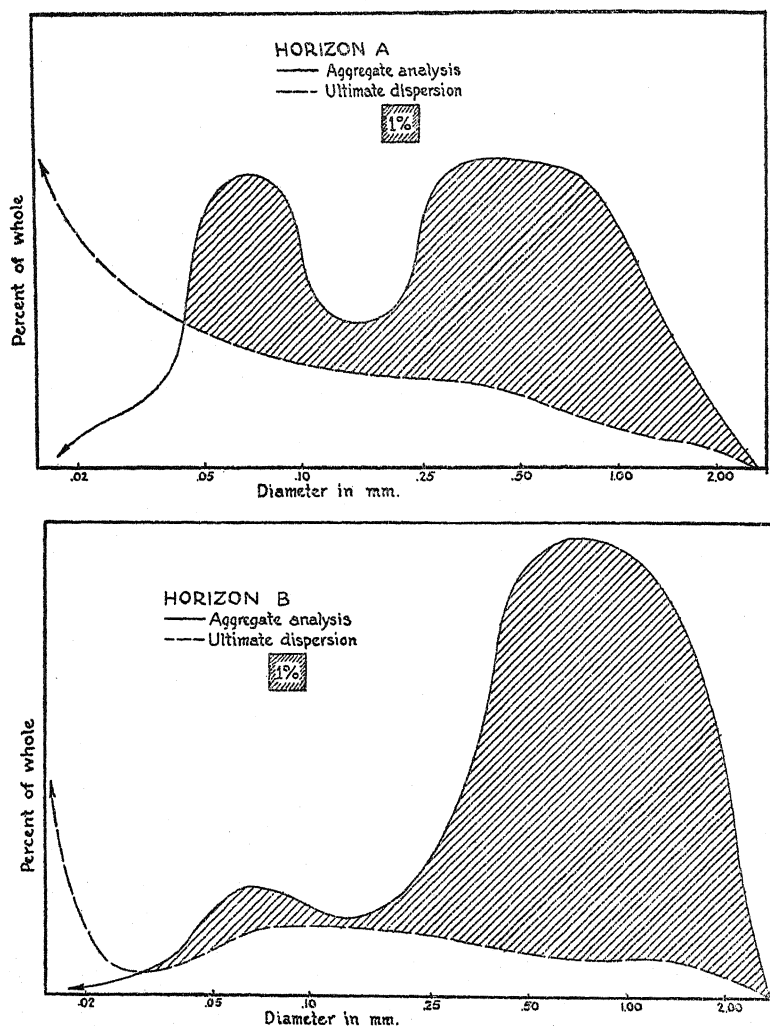


FIG. 2. SIZE-FREQUENCY DISTRIBUTION CURVE OF DAVIDSON CLAY WITH AND WITHOUT DISPERSION

91.9 per cent of the silt and clay is aggregated; in the Iredell only 74.2 per cent is in the form of granules larger in size than silt.

Neither the percentage of silt and clay aggregated nor the percentage of total

<sup>3</sup> Since the B horizon limits the permeability of the soil profile all discussion of aggregation will be limited to this layer except where otherwise indicated.

aggregates in the soil indicates the real differences between the two soils. If the B horizons are considered, it is observed that only 34.9 per cent of the silt and clay in the Iredell is aggregated into aggregates larger than 0.25 mm., whereas in the Davidson 87 per cent of the corresponding mechanical separates is in the form of large granules ( $> 0.25$  mm. in diameter). In other words, 149 per cent more of the silt and clay in the Davidson has been aggregated into large stable granules. Of the total aggregates present ( $> 0.05$  mm.) 94.6 per cent are larger than 0.25 mm. in diameter in the Davidson; in the Iredell only 46.9 per cent are of the larger size. An analysis of the entire profile shows that there is a more or less constant amount of aggregates in the Iredell from the surface downward. The Davidson, however, contains a higher percentage of large granules in the B horizon than in the A and C layers.

Examination of the granules with a wide field binocular microscope shows that the character of the aggregates in these soils is markedly different. The

TABLE 1  
*Dispersion and erosion ratios*

SOIL TYPE AND HORIZON	MIDDELETON METHOD		AGGREGATE METHOD*	
	Dispersion ratio	Erosion ratio	Dispersion ratio	Erosion ratio
Iredell A.....	16.5	14.1	34.0	29.1
Iredell B.....	12.1	9.5	25.8	20.2
Iredell C.....	34.2	32.2	40.0	27.8
Davidson A.....	3.6	2.3	17.1	10.8
Davidson B.....	2.6	1.2	8.5	4.0
Davidson C.....	3.6	2.9	17.7	14.4

\* In this method the dispersion ratio is = per cent silt + clay separated by aggregate analysis divided by total per cent silt + clay  $\times 100$ . The erosion ratio is this dispersion ratio divided by the colloid: moisture equivalent ratio.

Iredell aggregates appear to consist of a sand grain which is coated with a layer of silt and clay. These sand, silt, and clay particles which make up the secondary particles are held together by some cementing material, probably gelatinous silica. This same material cements the aggregates together, forming an impermeable soil layer.<sup>4</sup> When pressure is applied with the fingers to a cluster of these aggregates, they mold like putty except for the coarse, inner particle. They might be classed as "stone-fruit-like" aggregates. However, in the light of a recent classification of soil structure by Bayer (7) these secondary particles are not true granules and probably should be called "fragments."

The Davidson aggregates are composed of groups of smaller aggregates that crumble under pressure into smaller granules. They appear distinctly porous

<sup>4</sup> The swelling of the colloids undoubtedly plays an important rôle in the permeability of this layer. This will be discussed later.

under the microscope. They are true granules and may be referred to as the "pop-corn ball" type of aggregate.

### *Dispersion and erosion ratios*

The dispersion and erosion ratios by the Middleton method (23) agree somewhat with the aggregate analysis data as shown by table 1. The differences between the two soils are greater, however, than in the data reported by Middleton, the greater difference being shown by the erosion ratio. Because the erosion ratio is a more or less empirical factor it is difficult to visualize why any relationship should exist between the colloid:moisture equivalent ratio and the erosiveness of a soil. The dispersion ratio should give a better index of the erosiveness of a soil. Consequently, it will receive the greater emphasis in this discussion. The dispersion ratio as determined by Middleton is a measure of the stability of soil aggregates under the influence of moving water.

Since an aggregate analysis measures essentially the same effects, the data thus obtained were used to calculate this ratio. The values were always higher than by the Middleton method because the aggregate analysis caused a greater dispersion of the secondary particles due to the washing out of soluble flocculating electrolytes that are always present in the Middleton method. Moreover, some silt and clay are probably flocculated orthokinetically when using sedimentation methods; in an aggregate analysis such a possibility is eliminated.

### PROPERTIES OF THE COLLOIDS AFFECTING EROSION

Most of the physical and chemical properties of soils are dependent upon or associated with the colloidal fraction. In this investigation the physical properties of soils affecting erosion are interpreted in the light of a series of data upon the physicochemical properties of the extracted colloids when treated with various cations.

### *Chemical composition of the colloids*

The Davidson just barely is a lateritic soil (19) if a  $\text{SiO}_2\text{-Al}_2\text{O}_3$  ratio of 2 or less in the colloid fraction, as suggested by Harrassowitz, is used as the criterion for lateritization. The Iredell with a ratio of 2.49 is intermediate between the Davidson and the Putnam, which has a  $\text{SiO}_2\text{-Al}_2\text{O}_3$  ratio of 3.02 (11). Apparently the impervious nature of the Iredell profile has not permitted as rapid weathering as the more permeable Davidson soil. The decrease in the  $\text{SiO}_2\text{-Al}_2\text{O}_3$  ratio from the Putnam to the Davidson is accompanied by a decrease in the total cationic exchange capacity of the complex from 60 to 12 m.e. per 100 gm. of colloid. The magnitude of the charge on the particles has also been shown to decrease with the silica-sesquioxide ratio (1, 2, 20). Since the intensity of the charge of the colloidal particles is considered one of the main factors influencing the stability of colloidal suspensions, soils such as the Davidson should be expected to flocculate; soils with a ratio as high as the Putnam (3.02) should be stable.

*Stability of colloidal clay suspensions*

It was observed throughout this study that all colloidal suspensions of the Davidson were flocculated irrespective of the nature of the exchangeable cations on the complex. Only the H-, Ca-, and Ba-suspensions of the Iredell and Putnam were flocculated; these suspensions precipitated very slowly as compared with the Davidson soils. The flocculation time (table 2) was considered as that moment when a thin layer of supernatant liquid could be observed

TABLE 2

*The relation of different cations to the reaction, charge, and flocculation of several colloidal clays*

COLLOID AND TREATMENT	pH	ZETA POTENTIAL*	MIGRATION VELOCITY, MICRONS PER SEC. 1 VOLT PER CM.	FLOCCULATION TIME	VOLUME OF FLOC. AFTER 24 HOURS
		<i>millivolts</i>			<i>cc. per gm.</i>
H—Iredell.....	4.04	39.0	3.07	4 min.	5.2
Li—Iredell.....	6.91	42.1	3.31	Stable	
Na—Iredell.....	7.29	41.2	3.24	Stable	
K—Iredell.....	6.91	38.9	3.06	Stable	
Ca—Iredell.....	6.59	35.8	2.82	5 min.	6.0
Ba—Iredell.....	6.58	29.7	2.34	6 hrs.	7.2
H—Davidson.....	4.50	36.8	2.90	1 min.	4.0
Li—Davidson.....	6.85	40.5	3.19	2 min.	5.2
Na—Davidson.....	7.31	39.4	3.10	2 min.	5.4
K—Davidson.....	6.92	37.9	2.98	2 min.	5.4
Ca—Davidson.....	7.13	36.3	2.86	1 min.	3.0
Ba—Davidson.....	7.11	35.3	2.78	1 min.	3.2
H—Putnam.....	4.10	36.3	2.86	All stable after 24 hours; H, Ba, and Ca flocculated in about three days	
Li—Putnam.....	7.61	40.3	3.17		
Na—Putnam.....	7.66	38.5	3.03		
K—Putnam.....	7.32	38.7	3.05		
Ca—Putnam.....	6.96	35.0	2.75		
Ba—Putnam.....	6.86	32.6	2.56		

\* Credit is due Mr. R. F. Reitmeier for making the cataphoretic measurements.

above the suspension. The volume per gram of clay in the flocculated systems, the pH, and the zeta-potential and migration velocity of the colloidal particles are tabulated in table 2.

An analysis of these data and of associated factors throws much light on the relation of charge and hydration to the flocculation of colloidal clay suspensions. Kruyt (17) points out that the two factors influencing the stability of colloidal suspensions are the charge and the hydration of the dispersed particles. Wiegner (27) and Bradfield (10) consider that the magnitude of the charge of clay particles is due to the anionic nature (inner layer) of the colloidal complex and

that the potential increases or decreases directly with the extent of dissociation of cations from the colloidal surface.

Mattson (20), Anderson (1), and Anderson and Mattson (2) have shown that the charge and the exchange capacity of the colloid vary directly with the silica-sesquioxide ratio.

The charge of the Iredell, Davidson, and Putnam colloids was determined ultramicroscopically by means of a modification of the Tuorila cell (5). Suspensions of 0.0001 per cent by weight were used (19). The zeta-potential was calculated by the Helmholtz-Perrin equation, using the factor 4. The results with the Putnam sols agree with those reported by Bayer (5). The potentials follow the ionic series:  $\text{Li} > \text{Na} = \text{K} > \text{H} > \text{Ca} > \text{Ba}$ . The Li-, Na-, and K- Putnam sols were all stable, but the H-, Ba-, and Ca- systems flocculated very slowly. The intensity of the charge of the lateritic Davidson and that of the semi-lateritic Iredell colloids do not agree, however, with the data of Mattson, Anderson, and Anderson and Mattson. From the data of these investigators and others (10, 27) these colloids, especially the Davidson, would naturally be expected to have a lower negative charge than the Putnam. The negative potentials of all Iredell and Davidson sols were higher than those of the Putnam with the exception of the Ba-Iredell and the K-Davidson. It is difficult to explain these striking differences in the light of existing information. However, certain facts have been observed which may be used to explain partially these puzzling results.

The large differences in the hydration of the Davidson, Iredell, and Putnam colloids may affect the relative migration velocities of the particles. The method of calculating the zeta-potential from the Helmholtz-Perrin equation does not take into consideration the hydration of the particles. The data in table 3 show that the Putnam systems are more highly hydrated than those of the Iredell; the Davidson is not appreciably hydrated. The presence of a water shell around the particle might decrease the effectiveness of the "active points" on the surface of the colloid. Consequently, even though the Putnam colloid has five times as many "active points" (evidenced by its higher exchange capacity) as the Davidson, the high hydration of the Putnam might directly or indirectly impede the movement of the particles in an electric field.

Secondly, symmetry value (15) determinations show that the H ions are more easily replaced from the Davidson and Iredell colloids than from the Putnam. The symmetry values are:

	<i>Putnam</i>	<i>Iredell</i>	<i>Davidson</i>
With same clay concentration (KCl concentration = exchangeable H-ions) <i>per cent</i> .....	12.33	18.85	20.0
With same KCl concentration (same as exchangeable H ions) <i>per cent</i> .....	13.52	16.66	20.33

The values for the Putnam colloid agree very closely with those reported by Jenny (15) if allowance is made for slight differences in the clay concentrations. These results show that about 20 per cent of the replaceable H ions on the

Davidson colloid and only about 13 per cent of those on the Putnam colloid are exchanged by K ions at the symmetry concentration. In other words, the H ions on the Davidson are more active than those on the Putnam when considered on the basis of the total quantity present. Determinations of the pH values of the electrodyalyzed colloids also indicate that the clay acids in the Davidson and Iredell are more highly "dissociated" than the Putnam acid clay. Calculations based upon the pH values show that 1.26, 1.24, and 0.66 per cent of the total H ions present are "dissociated" in the Davidson, Iredell, and Putnam clays, respectively. If the "dissociation" of the Davidson is taken as 100, the Putnam and Iredell clay acids are 52.4 and 98.4 per cent "ionized," respectively. The symmetry values show that the exchangeable ions on the Putnam and Iredell colloids are only 61.4 and 94.4 per cent, respectively, as easily replaced as those on the Davidson. The two methods, therefore, give similar results and suggest that the potential of the Davidson colloid may be similar to the Putnam because of a greater activity of the exchangeable ions.

Thirdly, Lottermoser and Riedel (18) have shown that dilution of the positive  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{ThO}_2$  sols caused a reversal of charge; the sols were negatively charged in dilute concentrations. They attribute these results to an increase in dissociation with dilution and state that dilution and dialysis have the same effect on the intensity of the charge of colloidal particles. The sols used in the present investigation were rather dilute (0.0001 per cent) and, in the light of the dilution effect reported by Lottermoser and Riedel, the Davidson and Iredell colloids may exhibit a higher negative charge than would be expected in more concentrated systems.

The flocculation of the Davidson sols irrespective of the amount and nature of cations present, and in spite of a high zeta-potential, indicates that hydration is probably a more important factor influencing the stability of colloidal clay suspensions than is usually considered. The non-hydrated condition of lateritic soils such as the Davidson allows them to maintain a high state of granulation which, because of their inability to become hydrated, is not destroyed by the influence of water. Semi-lateritic and non-lateritic colloids such as the Iredell and Putnam are capable of becoming rather highly hydrated and, therefore probably form very unstable secondary particles except under extreme dehydration or in the presence of cementing materials such as organic matter. These results on the relative stability of the Iredell and Davidson colloids point out quite distinctly the reasons for the high degree of aggregation of the Davidson and the resistance of its granules to the dispersing action of run-off water.

#### *Hydration of colloidal clays*

Several methods of measuring the degree of hydration of soil colloids may be used, depending on whether the colloid is in the dry state or in suspension. Hydration can be determined by measuring the liquid intake of dry colloids (28). The significance of this type of water will be discussed in connection

with the swelling data. The relative hydration of different sols may be indirectly determined by calculations from viscosity data.

The water associated with the clay, as calculated from viscosity measurements, may consist either of a water "hull" around the clay particles (if completely dispersed) or of occluded water that is mechanically held between the

TABLE 3  
*The relation of exchangeable cations to the viscosity and swelling of several colloidal clays*

COLLOID AND TREATMENT	RELATIVE VISCOSITY	WATER OF HYDRATION*	LIQUID INTAKE		
			H <sub>2</sub> O	CaH <sub>2</sub>	Swelling
		cc. per gm.	cc. per gm.	cc. per gm.	cc. per gm.
H—Bentonite.....	7.00	35.00	3.77	1.45	2.32
Li—Bentonite.....	4.41	28.41	13.45	1.35	12.10
Na—Bentonite.....	3.41	24.11	12.27	1.20	11.07
K—Bentonite.....	2.92	21.31	9.76	1.20	8.56
Ca—Bentonite.....	3.42	24.16	4.00	1.50	2.50
Ba—Bentonite.....	6.51	33.96	3.90	1.40	2.50
H—Putnam.....	1.21	3.49	1.80	0.98	0.82
Li—Putnam.....	1.23	3.84	6.51	1.25	5.26
Na—Putnam.....	1.25	4.19	5.45	1.25	4.20
K—Putnam.....	1.24	4.04	1.46	0.96	0.50
Ca—Putnam.....	1.19	3.19	1.90	1.00	0.90
Ba—Putnam.....	1.20	3.34	1.74	0.90	0.84
H—Iredell.....	1.51	8.08	1.69	1.46	0.23
Li—Iredell.....	1.17	2.83	1.78	1.36	0.42
Na—Iredell.....	1.16	2.63	1.98	1.38	0.60
K—Iredell.....	1.18	2.98	1.53	1.51	0.02
Ca—Iredell.....	1.27	4.53	1.92	1.62	0.30
Ba—Iredell.....	1.26	4.33	1.86	1.50	0.36
H—Davidson.....	1.41	6.66	2.26	2.41	-0.15†
Li—Davidson.....	1.58	9.01	2.02	2.18	-0.16
Na—Davidson.....	1.51	8.06	1.90	2.08	-0.18
K—Davidson.....	1.77	11.41	1.93	2.35	-0.42
Ca—Davidson.....	1.31	5.11	1.94	2.22	-0.28
Ba—Davidson.....	1.35	5.76	2.08	2.43	-0.35

\* Calculated by the Mark and Meyer equation.

† The lower intake of water is due to a settling of the fluffy, dry colloid when wetted.

particles in a flocculated system. The thickness of the water hull undoubtedly is related to (a) the adsorptive capacity of the colloid for water molecules as affected by the nature of the inner layer and the amount and kind of exchangeable cations in the outer layer of the colloid and (b) the concentration of the sol. The amount of occluded water depends largely upon the degree of flocculation of the system, but is probably affected also by the hydration of the



flocculating cation. In systems such as the highly flocculated Davidson sols most of the water is probably held as occluded water. In thoroughly dispersed systems most of the hydration water is present as a shell around the colloidal particle. Calculations of the hydration water were made according to the Meyer and Mark modification (22) of the Einstein equation (17).

The data in table 3 show that the various cations do not affect the viscosity of different clays in the same order except that the viscosity of the H-, Ba-, and Ca- sols always ranked in the order named. The high content of water associated with a gram of clay in the Davidson systems and in the H-, Ca-, and Ba- Iredell sols is due to water of occlusion, since all of these sols were completely flocculated. The H-, Ba-, and Ca- Putnam sols flocculated so slowly that the amount of occluded water was probably very small. The data also show that the Li-, Na-, and K- Putnam colloids are about twice as highly hydrated as the corresponding Iredell systems. The chemical nature of the colloidal particle is undoubtedly responsible for these differences. Apparently, the inner layer of the Putnam colloid has a relatively high polarizing effect on the water molecules. All bentonite sols were extremely viscous indicating that the chemical nature of the alumino-silicate particle must have a pronounced effect upon the hydration of the particle. Bentonite has an exchange capacity of about 90 m.e. per 100 gm. of colloid.

*Swelling of soil colloids.*—Numerous investigators have noted a certain relationship between swelling and other properties of soil colloids. Bennett (9) observed that soils with a low silica-sesquioxide ratio were more friable, permeable, and resistant to erosion than those with a high ratio, and that the friable soils showed no visible swelling or shrinking even at extreme moisture variations. Soils with a high  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratio were subject to wide changes in volume during drying or wetting. Anderson (1) found that swelling increased with the  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratio and that Na-saturated clay swelled about twice as much as K- clay. Additions of Ca ions to the Na- clay decreased the amount of swelling. Mattson (21) studied the effect of adsorbed cations on the swelling of soils and found that swelling decreased according to the ionic series:  $\text{Na} > \text{K} > \text{Ca} > \text{Mg} > \text{H} > \text{methylene blue}$ . Winterkorn and Baver (28) have reported that the total amount of water taken up by the colloidal clays increased with the  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratio. They also show that water intake extends over a longer period of time in soils with a high  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratio.

The swelling data in table 3 were obtained by the method of Winterkorn and Baver (28). The order of swelling of the different clays is: Bentonite<sup>5</sup> > Putnam<sup>5</sup> > Iredell > Davidson, with the latter exhibiting no swelling. The  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratios of these colloids decrease in the same order. Baver and Winterkorn<sup>6</sup> have shown that the swelling of any given colloid varies with the

<sup>5</sup> The swelling data on the bentonite and Putnam colloids were obtained by H. F. Winterkorn (28).

<sup>6</sup> Baver, L. D., and Winterkorn, H. F., University of Missouri, unpublished data compiled, 1934.

nature of the cations on the exchange complex. In bentonite swelling followed the ionic series:  $Li > Na > K > Ca = Ba > H$ ; in Putnam clay the series was:  $Li > Na > Ca > Ba > H > K$ ; in Iredell the series was:  $Na > Li > Ba > Ca > H > K$ ; the Davidson exhibited no swelling irrespective of the nature of the exchangeable cations present. The low swelling of the K-saturated Iredell colloids confirms the results of Baver and Winterkorn<sup>6</sup> with other K-saturated clays. Moreover, their observations concerning the relative differences between the swelling of Ca- and H- saturated systems are confirmed by the behavior of the Ca- and H- Iredell colloids. The practical significance of these results is mentioned in the general discussion of this paper. The data distinctly point out that the hydration of clays is to a great extent determined by the chemical nature of the clay particle and that colloidal clays behave differently in their swelling from bentonite.

The swelling data partly explain the differences between the rate of percolation of water through the Iredell and Davidson soils and the extent to which the soils are aggregated into stable granules.

Inasmuch as the Davidson colloid does not swell in the presence of water one should expect the soil to have a relatively high permeability for water; the aggregates should be more stable than those secondary particles that increase in volume when wetted. Consequently, on the basis of hydration alone, the Davidson soil should be more resistant to the erosive action of water than the Iredell.

#### *Permeability of colloidal clay membranes*

The permeability of a soil profile is controlled largely by the amount and state of dispersity of the colloidal material present. Many soils with a highly colloidal B-horizon such as the Iredell and Putnam, are only slightly permeable to water; other soils, however, such as the Davidson with just as high a colloid content are extremely permeable: Bennett (9) observed that certain lateritic soils with a very high clay content were decidedly permeable to water and could be cultivated soon after heavy rains; these permeable clay soils apparently were not highly hydrated. Antipov-Karatajev (3) observed that soils saturated with iron were very permeable. Baver (5) studied the rate of ultrafiltration through Na- and Ca-colloidal clay membranes and calculated the size of the pores in the membranes on the basis of the rate of filtration. The pores in the Ca- clay membranes were found to be 8.3 times larger than those in the Na- clay.

In the present investigation the permeabilities of colloidal clay membranes<sup>7</sup> of the Iredell, Davidson, Putnam, and Bentonite colloids, when treated with various cations, were studied.

The data (fig. 3 to 5 inclusive) show a segregation of the curves into two groups as far as the effects of the exchangeable cations are concerned. The

<sup>7</sup> See (19) for method of preparation of membranes.

one group contains the Li-, Na-, and K- sols, and the other, the H-, Ba-, and Ca systems. This division is very pronounced with the Iredell. Apparently, the rate of ultrafiltration is related to the degree of flocculation, the more flocculated systems being more permeable than the dispersed. Since all of the Davidson sols are flocculated, the rates of filtration are somewhat similar. Qualitative tests of the rate of filtration through a glass filter under a pressure of one atmosphere showed that all the Davidson systems and the H-, Ba-, and Ca- Iredell sols flocculated and that the volumes of the flocs formed remained practically constant until the supernatant liquid had been removed. The volume of the floc then decreased under the applied pressure, resulting in the squeezing out of occluded water from the loosely held flocules. The filtra-

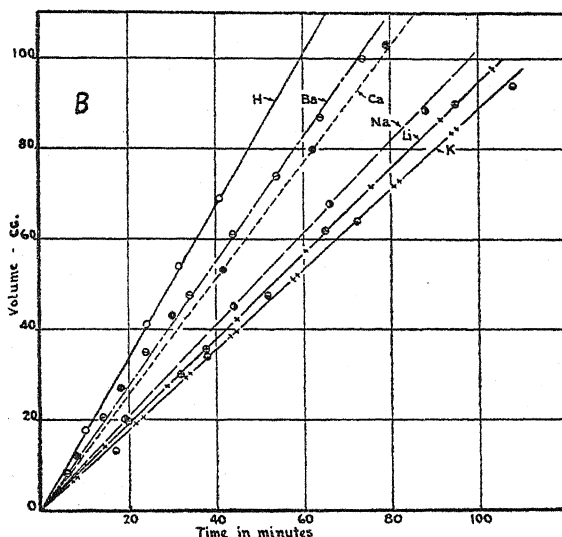


FIG. 3. EFFECT OF DIFFERENT CATIONS UPON THE PERMEABILITY OF DAVIDSON CLAY MEMBRANES

tion up to this point apparently proceeded more or less as a water displacement. This resulted in a constant rate of filtration until the last few cubic centimeters of intermicellar liquid were removed. Packing of the clay membrane by removal of occluded water then caused a decrease in the rate of percolation in the more hydrated systems such as the Ba- and H-Iredell; in the weakly hydrated systems such as the Davidson the rate of filtration remained constant until all of the intermicellar liquid had been removed.

The permeability of the membranes formed from 1 gm. of clay or bentonite follows the definite order of  $H > Ba > Ca$  which is the same as that of their relative viscosity. In the Iredell and Putnam colloids and in the bentonite, the order of the alkali cations was  $K > Na > Li$ ; in the Davidson the order was  $Na > Li > K$ . No definite relationship existed between the swelling and

the permeability of the various clay membranes if all systems are considered. If, however, only the H-, Ca-, and Ba- systems are considered, permeability

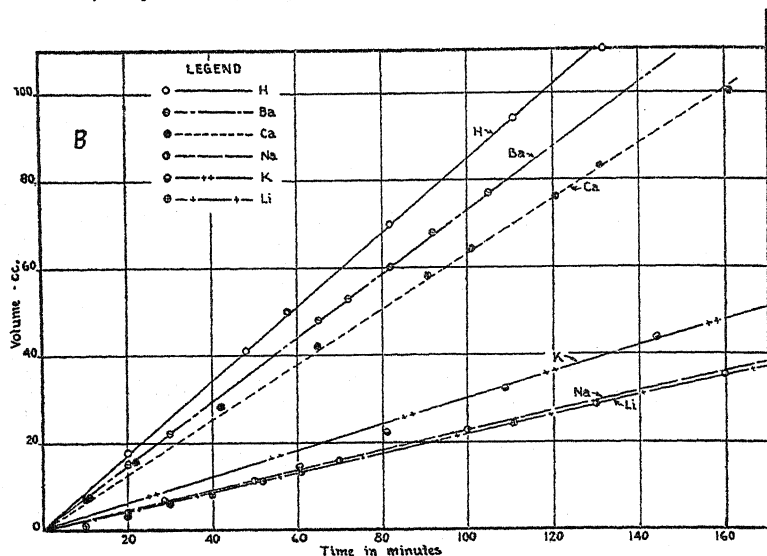


FIG. 4. EFFECT OF DIFFERENT CATIONS UPON THE PERMEABILITY OF IREDELL CLAY MEMBRANES

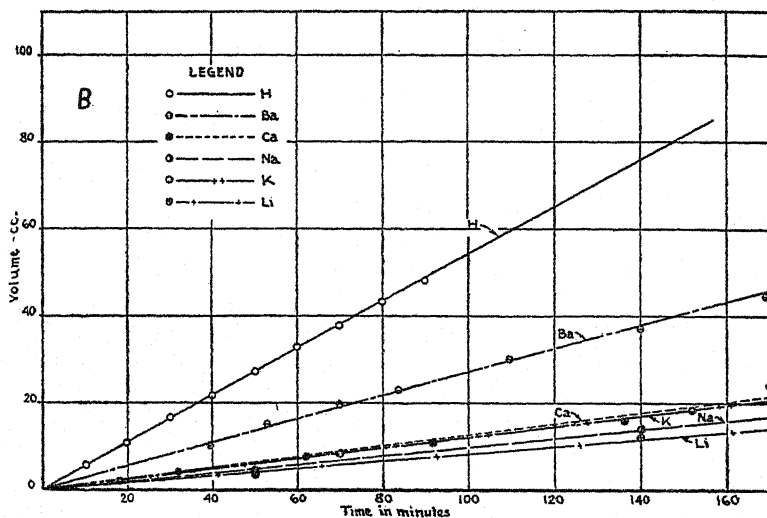


FIG. 5. EFFECT OF DIFFERENT CATIONS UPON THE PERMEABILITY OF PUTNAM CLAY MEMBRANES

is inversely related to the amount of swelling. This is true with all colloids except the Iredeell, in which the differences in swelling of the various sols is

very small. Such a relationship should naturally be expected, since swelling results in a decrease in the effective pore volume of the clay. H-clays were found to swell less than Ca- and Ba- clays; and the H- systems were more permeable than those saturated with Ca and Ba ions. Apparently, the formation of granules that do not change their volume when wetted is an important factor in soil permeability. The fact that H- clays swell less and are more permeable than Ca- saturated clays throws considerable doubt upon the direct effect of liming acid soils on soil granulation and permeability.

It is noted that K-saturated clays occupy an intermediate position between the Na- and Li- systems and those saturated with H, Ca, and Ba ions. The higher permeability of the K- clays over the Na- and Li- systems is due to the low swelling of the former. Since the K- colloids are dispersed their relative

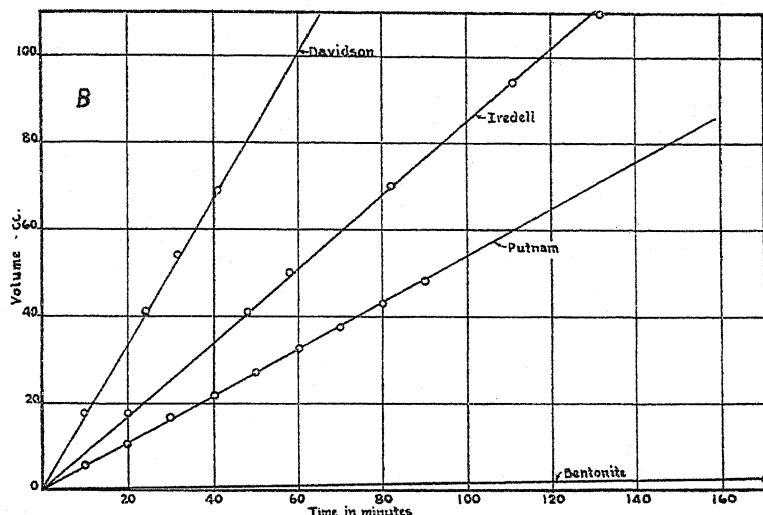


FIG. 6. PERMEABILITY OF DIFFERENT H-CLAY MEMBRANES

permeabilities are not so high as the flocculated H- and Ba- suspensions. The data showing the effect of the exchangeable cations on the permeability of clay membranes indicate that the rate of percolation is dependent upon the degree of dispersion and the extent of swelling of the colloids.

Comparisons of the effect of the chemical nature of the colloidal complex on the permeability of clay membranes are shown in figures 6 to 8 inclusive. These results show that irrespective of the nature of the adsorbed cation the order of permeability for the different colloids is: Davidson > Iredell > Putnam > bentonite. This order is just the reverse of the swelling and of the  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratios of these colloids. These data point out quite distinctly that the nature of the inner layer has a marked effect upon the hydration of the colloidal particle. The effect of the exchangeable cations appears to be only of secondary importance. Studies on the colloidal material extracted from

the non-erosive Davidson and the erosive Iredell soils have shown that the hydration and state of dispersion of the colloids are important factors in

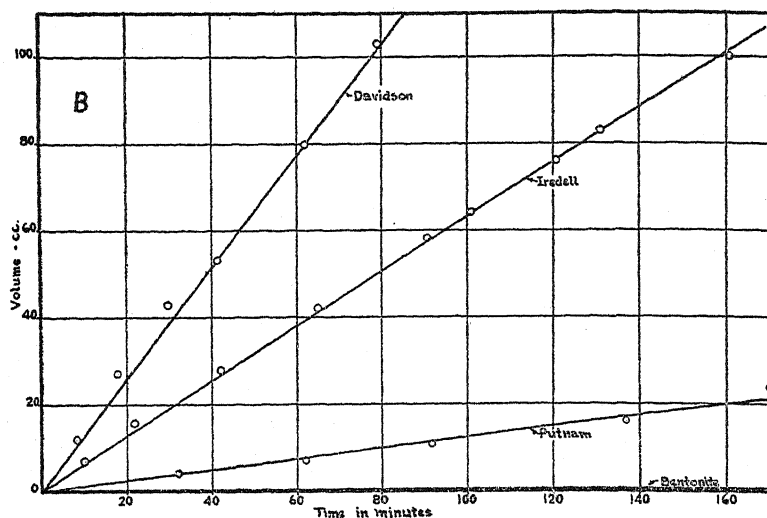


FIG. 7. PERMEABILITY OF DIFFERENT Ca-CLAY MEMBRANES

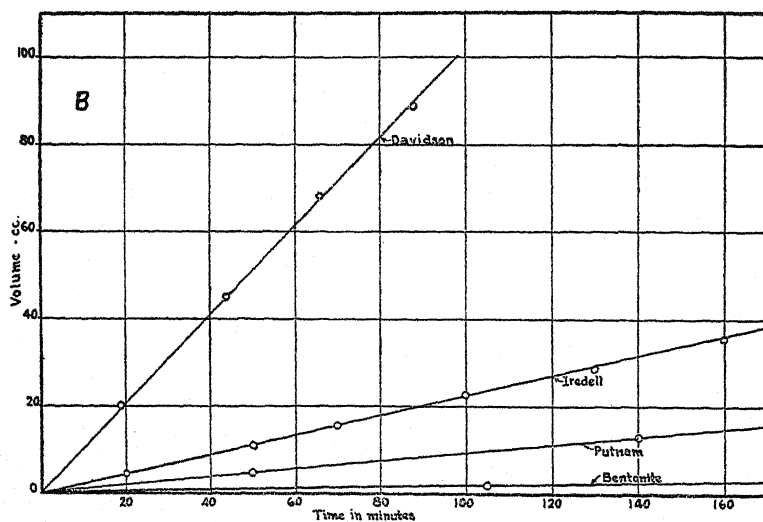


FIG. 8. PERMEABILITY OF DIFFERENT Na-CLAY MEMBRANES

determining the differences in the erosiveness of the two soils. The resistance of the Davidson clay to erosion can be attributed to the non-hydrated and granular condition of the colloidal fraction. Consequently, rapid percolation

of water through the profile is permitted, which in turn reduces the amount of surface run-off and erosion. The relative rates of percolation through the Davidson and Iredell clay membranes are conclusive evidence of the greater permeability of the Davidson soil. The dense, impermeable membranes formed by the Iredell colloid (19) indicate quite clearly that the permeability of the B horizon of this soil is due to the hydrated and deflocculated state of the colloids present. The investigation of the stability, hydration, and permeability of the colloids extracted from these soils has made possible a clearer concept of the effect of the physical properties of soils on erosion.

#### DISCUSSION

A laboratory study of the physical properties of several soils, found under the same environmental conditions, shows that their difference in erodibility is due primarily to the degree of aggregation of the finer fractions. The Davidson clay, a relatively non-erosive soil, is highly aggregated into large aggregates, whereas the Iredell sandy clay loam, a very erosive soil, contains a lower content of much smaller aggregates. The aggregates of the erosive soil are dense, impermeable, and less stable than the large aggregates of the Davidson. These differences manifest themselves in the physical condition of the soil; the B horizon of the Davidson is friable, granular, porous, and permeable to water, whereas the B layer of the Iredell is distinctly plastic, sticky, and impermeable. Suspension of Davidson colloids flocculated irrespective of the nature of the adsorbed cation, or of the amount of NaOH up to 150 per cent saturation, but only the H-, Ca-, and Ba- Iredell colloids flocculated.

No definite relationship existed between the zeta potential and the  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratio of the colloids. This was unexpected in the light of other work but is possibly explained by the fact that the clay acids with low  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratios were more highly dissociated than those with higher ratios, as shown by pH and symmetry value measurements and by the fact that those colloids with low ratios were less hydrated. The Davidson colloids do not swell, irrespective of the nature of the exchangeable cations present; the Putnam and Iredell, however, become hydrated, the Putnam more than the Iredell. These data on charge and hydration of the various clay sols suggest very strongly that hydration is a more important factor than charge in determining the stability of clay suspensions.

Calculations from viscosity measurements of the hydration of the various sols showed that the Putnam was more highly hydrated than the Iredell. The Davidson sols showed a high content of water associated with the clay, but since the swelling determinations showed that it was non-hydrated, and since these sols were all flocculated, it is reasonable to assume that this was occluded water. Swelling was greatest in the Li- and Na- and lowest in the K- systems. In the other systems the order was  $\text{Ca} > \text{Ba} > \text{H}$ . Since the swelling of these latter systems is inversely related to their viscosity and relative flocculation time, it appears that the degree of aggregation has considerable influence on the amount of swelling.

Permeability measurements of the clay membranes show that the highly dispersed and hydrated systems are more impermeable than the flocculated and only slightly hydrated systems. The H- clays of all soils were more permeable than the Ca- clays. This, in addition to the greater swelling of the Ca- systems, makes it very questionable as to whether lime has any direct beneficial effect on the physical condition of acid soils. Any improvement in the physical properties of the soil is probably indirect through an increase in the organic matter content of the soil, resulting in the formation of more stable granules.

These data on the flocculation, hydration, and permeability of the Iredell and Davidson colloids explain partially, at least, the differences in their erosiveness.

#### SUMMARY

The erosiveness of the Iredell is due to its ease of dispersion and to the dense, impervious nature of the B horizon. Hydration is an important factor in its dispersion.

The non-erosive nature of the Davidson clay is due to the non-hydrated condition and the high degree of flocculation of the colloidal fraction into large porous and stable aggregates.

The Davidson colloids flocculated irrespective of the kind of exchangeable cations on the complex, whereas only the H-, Ca-, and Ba- Iredell systems flocculated.

Electrokinetic potentials of the Iredell, Davidson, and Putnam sols were practically the same, indicating that hydration, rather than charge, was the main contributing factor to stability of the suspensions.

Swelling was in the order Bentonite > Putnam > Iredell > Davidson. . . This is the reverse of the  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratios.

The K, Na, and Li cations showed no definite order of effect on the swelling of the colloids. The Ca, Ba, and H decreased swelling in the order named.

Permeability of the different clay membranes was in the order: H > Ba > Ca > K > Na > Li.

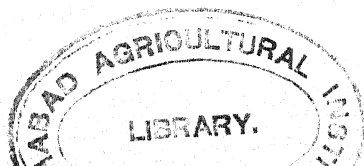
These physicochemical properties of the colloids are paramount factors influencing the erosiveness of soils.

#### REFERENCES

- (1) ANDERSON, M. S. 1929 The influence of substituted cations on the properties of soil colloids. *Jour. Agr. Res.* 38: 565-584.
- (2) ANDERSON, M. S., AND MATTSO, S. 1926 Properties of the colloidal soil material. U. S. Dept. Agr. Bul. 1452.
- (3) ANTIPOV-KARATAJEV, I. N. 1930 Ueber die Anwendung der Filtrationsanalyse bei der Untersuchung der für die Bodendispersitat massgebenden Faktoren. *Kolloidchem. Beihefte* 31: 374-417.
- (4) BARTELL, F. A. 1921 Progress Report on Soil Erosion Experiments. Bureau of Public Roads, U. S. Dept. Agr. in cooperation with N. C. Dept. Agr.



- (5) BAVER, L. D. 1929 The effect of the amount and nature of exchangeable cations on the structure of a colloidal clay. *Missouri Agr. Exp. Sta. Res. Bul.* 129.
- (6) BAVER, L. D. 1933 Soil porosity as an index of structure. *Proc. Amer. Soil Survey Assoc. Bul.* 14: 83-85.
- (7) BAVER, L. D. 1934 A classification of soil structure and its relation to the main soil groups. *Proc. Amer. Soil Survey Assoc. Bul.* 15: 107-109.
- (8) BAVER, L. D., AND RHOADES, H. F. 1932 Aggregate analysis as an aid in the study of soil structure relationships. *Jour. Am. Soc. Agron.* 24, pp. 920-930.
- (9) BENNETT, H. H. 1926 Some comparisons of the properties of humid-tropical and humid-temperate American soils, with special reference to the indicated relations between chemical composition and physical properties. *Soil Sci.* 21: 349-375.
- (10) BRADFIELD, RICHARD 1923 The nature of the chemical reactions of colloidal clay. *Colloid Symposium Monog.* 1: 369-383.
- (11) BRADFIELD, RICHARD 1925 The chemical nature of colloidal clay. *Jour. Amer. Soc. Agron.* 17: 253-270.
- (12) BURR, W. W., AND RUSSEL, J. C. 1927 The importance of organic matter in soil structure and tilth. *Abs. Proc. First Internatl. Cong. Soil Sci.* 1: 67.
- (13) DICKSON, R. E. 1929 The results and significance of the Spur (Texas) run-off and erosion experiments. *Jour. Amer. Soc. Agron.* 21: 415-423.
- (14) JANOTA, R. 1928 Ueber die Draintiefen in verschiedenen Bodentypen. *Proc. First Internatl. Cong. Soil Sci.* 4: 737-745.
- (15) JENNY, HANS 1932 Studies on the mechanism of ionic exchange in colloidal aluminum silicates. *Jour. Phys. Chem.* 36: 2217-2258.
- (16) JENNY, HANS 1933 Soil fertility losses under Missouri conditions. *Missouri Agr. Exp. Sta. Bul.* 324.
- (17) KRUYT, H. R. (Trans. by H. S. VAN KLOOSTER) 1930 Colloids. John Wiley and Sons, New York.
- (18) LOTTERMOSER, A., AND RIEDEL, W. 1930 Ueber die Ladung von Kolloidteilchen und ihre Beeinflussung. *Kolloid Ztschr.* 51: 30-39.
- (19) LUTZ, J. F. 1934 The physico-chemical properties of soils affecting soil erosion. *Missouri Agr. Exp. Sta. Res. Bul.* 212.
- (20) MATTSON, SANTE 1926 The relation between the electrokinetic behavior and the base exchange capacity of soil colloids. *Jour. Amer. Soc. Agron.* 18: 258-270.
- (21) MATTSON, SANTE 1928 The influence of the exchangeable bases on the colloidal behavior of soil materials. *Proc. First Internatl. Cong. Soil Sci.* 2: 185-198.
- (22) MEYER, K. H., AND MARK, H. 1930. Der Aufbau der hochpolymeren organischen Naturstoffe. Akad. Verlagsges, Leipzig.
- (23) MIDDLETON, H. E. 1930 Properties of soils which influence soil erosion. U. S. Dept. Agr. Tech. Bul. 178.
- (24) MIDDLETON, H. E., ET AL. 1932 Physical and chemical characteristics of the soils from the erosion experiment stations. U. S. Dept. Agr. Tech. Bul. 316.
- (25) MILLER, M. F., AND KRUSEKOPF, H. H. 1932 The influence of cropping and methods of culture on surface run-off and soil erosion. *Missouri Agr. Exp. Sta. Res. Bul.* 177.
- (26) SLATER, C. W., AND BYERS, H. G. 1931 A Laboratory Study of the Field Percolation Rates of Soils. U. S. D. A. Tech. Bul. 282.
- (27) WIEGNER, G. 1924 Dispersitat und Basenaustausch. *Proc. 4th Internatl. Soc. Soil Sci.* Comn. 2: 390-424.
- (28) WINTERKORN, H. F., AND BAVER, L. D. 1934 Sorption of liquids by soil colloids: I. Liquid intake and swelling by soil colloidal materials. *Soil Sci.* 38: 291-298.





# THE INFLUENCE OF EXCHANGEABLE SODIUM IN THE SOIL ON ITS PROPERTIES AS A MEDIUM FOR PLANT GROWTH

E. I. RATNER

*Scientific Research Institute for Fertilizers, Moscow, U. S. S. R.*

Received for publication March 4, 1935

The experimental work reported in this paper deals with the problem of the influence of increasing amounts of exchangeable sodium in the soil on plant growth and on the physical properties of soils.

## EXPERIMENTAL

The first experiment on the influence of exchangeable sodium in the soil on plant growth was carried out by the author in 1930, with chernozem soil, into which was introduced 33.4 m.e. of exchangeable sodium per 100 gm. of soil, representing 71 per cent of the total exchangeable bases. This was obtained by treating the soil with a normal solution of NaCl, with subsequent removal of the salt first with water and then by dialysis. After these treatments the soil contained the quantity of exchangeable sodium mentioned and but traces of chloride ion. The water suspension of the soil had a pH of 7.6.

Each of two 250-gm. samples of the artificial solonetz obtained in this way, was carefully mixed with 1,200 gm. of washed quartz sand, fertilized with Hellriegel's mixture, and placed in small containers suitable for the growing of plants. To two other weighed samples, besides Hellriegel's mixture, gypsum was added in an amount proportional to the exchangeable sodium.

Oats were planted in these receptacles. In those containing no gypsum the seeds germinated very slowly and died almost immediately. But in the containers to which gypsum had been added the plants developed normally and gave a normal yield.

It thus appeared that 33.4 m.e. of exchangeable Na, amounting to 71 per cent of the total of exchangeable bases, in this chernozem soil was fatal to the plants, notwithstanding the fact that they were fully provided with nutritive substances in the form of Hellriegel's mixture and in spite of a six-fold dilution of the soil with sand.

The experiment with the chernozem soil was repeated in greater detail. In order to create in the soil various relations between the exchangeable forms of calcium and sodium, the soil was first treated with 0.05 *N* HCl until all the exchangeable bases were removed, and then, after complete removal of HCl, it was treated with a diluted solution of NaOH and Ca(OH)<sub>2</sub> in various proportions calculated to satisfy the total exchange capacity of the soil, equal to 52 m.e. per 100 gm. of soil.

After a 10 days' reciprocal action of the soil with the reagents introduced, the excess of fluid was evaporated in the air, and the soil was dried, ground in a mortar, and passed through a 1-mm. sieve.

With the soils obtained in this way pot experiments were carried out in small containers holding 600 gm. of soil each. To each container were added 0.2 gm. N and 0.2 gm.  $K_2O$  (mixture of  $KNO_3 + NH_4NO_3$ ) and 0.1 gm.  $P_2O_5$  (double superphosphate).

In 1933 the experiment was carried out with oats. In 1934 spring wheat was sown on the same containers, and half doses of the fertilizers indicated were again introduced.

In table 1 are shown the yield data for both years and also the pH of the soil (in water) before the start of the experiment. Plate 1 shows the wheat in this experiment.

As seen from table 1 in this experiment also, the substitution of about 70 per cent of the exchange capacity of the soil by sodium proved fatal to the

TABLE 1

*The influence of increasing amounts of exchangeable sodium in the soil on the growth of oats and wheat*

SOIL CONTENT OF EXCHANGEABLE Ca-Na IN PERCENTAGES OF THE TOTAL EXCHANGE CAPACITY	pH OF WATER SUSPENSION	YIELD OF OATS, AIR-DRY BASIS	YIELD OF WHEAT, AIR-DRY BASIS
		gm.	gm.
100 per cent Ca.....	6.68	14.9	17.6
85 per cent Ca + 15 per cent Na.....	6.73	14.7	16.9
70 per cent Ca + 30 per cent Na.....	7.11	15.4	17.0
50 per cent Ca + 50 per cent Na.....	7.32	13.2	14.5
30 per cent Ca + 70 per cent Na.....	7.86	Plants died soon after germination	

plants, whereas the replacement by the latter of up to 50 per cent of the total exchangeable bases resulted in only a delay in the germination of the seeds and was reflected to a much smaller degree in the yield.

Further experiments in this direction were made with natural non-carbonate solonetz of the zone of chestnut soils of the European part of the U.S.S.R.

The soils for the experiments were from horizon A (upper elluvial horizon, 15-20 cm. thick) and from horizon  $B_1$  (the illuvial horizon [columnar] lying lower, 15 to 20 cm. thick). Some of the characteristics of these soils are shown in table 2. In all the soils the horizon of effervescence lies lower than  $B_1$ .

In order to remove the exchangeable sodium, the soils were treated with gypsum, introduced in somewhat greater amounts than were apparently necessary from the calculation of exchangeable sodium, and further they were washed several times with water, in order to remove the products of reaction. The control soils were washed with water in order to equalize the possible action of the washing itself.

With the soils thus obtained pot experiments were conducted. On the first

soil mentioned in table 2, oats were grown; on the second, spring wheat; and on the third, barley.

In order to satisfy the nutritive requirements of the plants, to each vessel, containing 4–5 kl. of soil, were added: 0.5 gm. N and 0.5 gm.  $K_2O$  ( $NH_4NO_3 + KNO_3$ ), and 0.1 gm.  $P_2O_5$  (double superphosphate).

In table 3 the yield data of this experiment are correlated with the content of exchangeable Na in the soil. As seen from table 3, the replacement of sodium by calcium led to no marked increase of yield, either in horizon A, in which the

TABLE 2  
*Characteristics of the alkali soils taken for experiment*

SOIL	TOTAL HUMUS	TOTAL ALKALINITY IN $HCO_3^-$	pH IN WATER	$Cl^-$	$SO_4^{--}$	TOTAL EXCHANGEABLE BASES	EXCHANGEABLE Na	
							Per 100 gm. of soil	Proportion of total exchange bases
	per cent	per cent		per cent	per cent	m.e.	m.e.	per cent
Deep-columnar solonetz of the Valuisk Experiment Station (Lower Volga):								
Horizon A.....	2.70	0.053	6.94	0.02	Trace	23.5	4.6	19.7
Horizon B <sub>1</sub> .....	1.43	0.070	7.98	0.07	Trace	30.1	10.1	33.6
Deep-columnar solonetz of the Saratov Experiment Station (Lower Volga):								
Horizon A.....		0.024	7.10	0.04	Trace	21.2	2.2	10.4
Horizon B <sub>1</sub> .....		0.066	7.63	0.06	Trace	32.6	8.5	26.0
Strongly solonetzic soil from the Chongar Peninsula (South of Ukraine, on the border of Crimea):								
Horizon A.....	2.34	0.023	6.98	0	Trace	13.9	2.6	18.7
Horizon B <sub>1</sub> .....	2.25	0.064	7.78	Trace	Trace	24.5	11.0	45.0

content of exchangeable Na is small, or in horizon B<sub>1</sub>, containing considerable amounts of exchangeable sodium, up to 45 per cent of the exchange capacity.

Thus, the pot experiments indicate that within limits a high content of exchangeable sodium in the soil is not in itself detrimental to the normal development of plants. As has been shown, in the chernozem soil, rich in organic matter (9–10 per cent humus), the limit destructive to the plants occurred when from 50 to 70 per cent of the total exchangeable bases was replaced by sodium. Experiments with artificial substrata—artificial humic acid and permutite—completely saturated with sodium indicate that in the case of a soil poor in organic matter, the limit in the content of exchangeable sodium that can be endured by the plant is still higher.

In these experiments, humic acid and permutite saturated with sodium and equivalent in exchange capacity were introduced into sand cultures in which oats supplied with Hellriegel's nutritive mixture were growing. In the

TABLE 3  
*Influence of exchangeable Na in the soil on plant growth*

SOILS	CONTENT OF EXCHANGEABLE Na IN PERCENTAGE OF THE TOTAL EXCHANGEABLE BASES	DRY MATTER YIELD PER VESSEL	
		Soil washed with water only	Soil treated with gypsum and washed with water
		gm.	gm.
Deep-columnar solonetz of the Valuisk Experiment Station:			
Horizon A .....	19.7	37.8	37.3
Horizon B <sub>1</sub> .....	33.6	18.8	19.5
Deep-columnar solonetz of the Saratov Experiment Station:			
Horizon A .....	10.4	34.7	34.9
Horizon B <sub>1</sub> .....	26.0	17.8	18.2
Strongly solonetzic soil from Chongar Peninsula:			
Horizon B <sub>1</sub> .....	45.0	25.0	25.3

TABLE 4  
*The influence of exchangeable sodium in the soil on some of its properties*

CONTENT OF EXCHANGEABLE SODIUM	pH	DISPER-SION-PARTICLES <0.001 MM.	RATE OF CAPILLARY RISE OF WATER WHEN PACKING THE SOIL INTO GLASS TUBES TO A HEIGHT OF 12 CM.
		per cent	
Check* .....	6.2	1.4	During 4 hrs. 20 min. the water rose continuously
0.9 m.e., or 1.9 per cent of total exchangeable bases .....	6.9	1.9	During 9 hrs. 5 min. the water rose continuously
5.1 m.e., or 10.6 per cent of total exchangeable bases .....	7.2	9.0	During 20 days the water rose 8.5 cm.
20.5 m.e., or 42.7 per cent of total exchangeable bases .....	7.4	26.4	During 20 days the water rose 2.2 cm.
33.4 m.e., or 70.6 per cent of total exchangeable bases .....	7.6	29.1	During 20 days the water rose 1.8 cm.

\* Original soil, containing no exchangeable sodium, washed with water.

first year, the plants perished after the introduction both of humic acid and of permutite. In the second year the plants perished after the introduction of humic acid, whereas after permutite they developed normally and gave a yield approaching that following the use of permutite plus gypsum.

If we attempt to apply to field conditions the data obtained from pot cultures we must introduce an essential correction, for the physical properties of soil substantially change when even comparatively small amounts of exchangeable sodium are introduced. This may be seen in table 4 and in figure 1, in which is shown the change in dispersion, in rate of capillary rise of water, and in filterability of the chernozem soil artificially enriched by increasing amounts of exchangeable sodium. This was done by treating the soil with a solution of NaCl of various concentrations, with subsequent removal of the salts with water and then by dialysis.

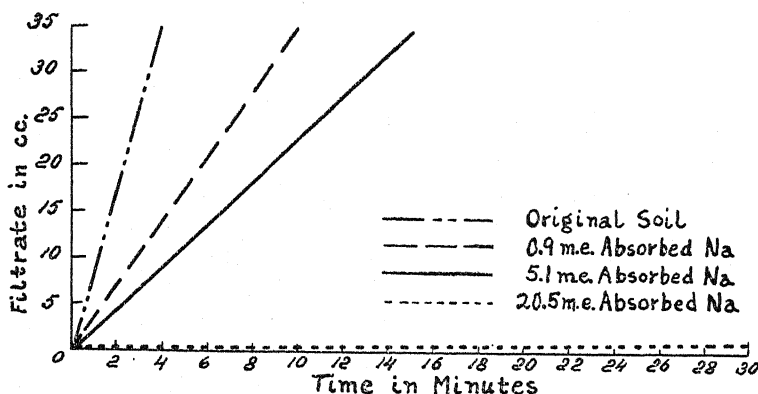


FIG. 1. INFLUENCE OF INCREASING AMOUNTS OF EXCHANGEABLE SODIUM UPON THE FILTERABILITY OF CHERNOZEM SOIL

TABLE 5

*The effect of 2 and 3 years' application of various types of nitrogen fertilizers on the rate at which the water in the soil rises to a height of 12 cm. by capillary attraction*

FERTILIZER	AFTER 2 YEARS' APPLICATION	AFTER 3 YEARS' APPLICATION
1. KP.....	4 hrs.	8 hrs., 10 min.
2. KP + NaNO <sub>3</sub> .....	8 hrs., 40 min.	20 hrs.
3. KP + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .....	4 hrs.	5 hrs., 30 min.
4. KP + CO(NH <sub>2</sub> ) <sub>2</sub> .....	3 hrs., 45 min.	7 hrs., 20 min.
5. KP + CaCN <sub>2</sub> .....	3 hrs., 50 min.	5 hrs., 50 min.

The replacement by sodium of 10.6 per cent of the total exchangeable bases (5.1 m.e.) produced a desired change in the physical properties of the soil. Even the replacement by sodium of only 1.9 per cent (0.9 m.e.) of the total exchangeable bases influenced these properties.

The deleterious effect of relatively small amounts of exchangeable sodium on the physical properties of chernozem soil was further confirmed by another experiment performed during a study of the effect of various types of nitrogen fertilizers on pot cultures. Nitrogen fertilizers—NaNO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, CO(NH<sub>2</sub>)<sub>2</sub>, and CaCN<sub>2</sub>—were introduced annually for 3 years into the same

soil sample, which was planted to oats. These fertilizers, in addition to superphosphate and  $K_2SO_4$ , were added at the rate of 0.5 gm. of nitrogen for each pot containing 5 kgm. of soil. The soil used was the same chernozem as in the previous experiment. At the end of the second and third years of the experi-

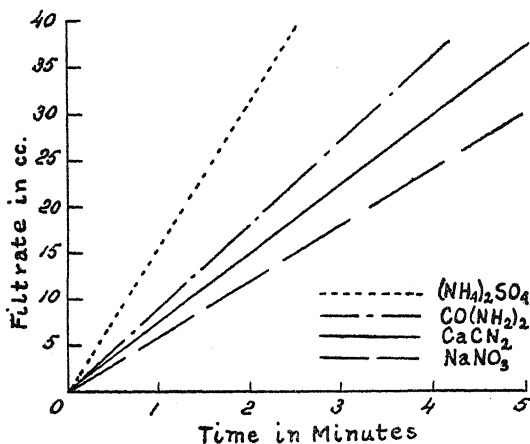


FIG. 2. EFFECT OF THREE YEARS' APPLICATION OF VARIOUS TYPES OF NITROGEN FERTILIZERS ON THE FILTERABILITY OF THE SOIL

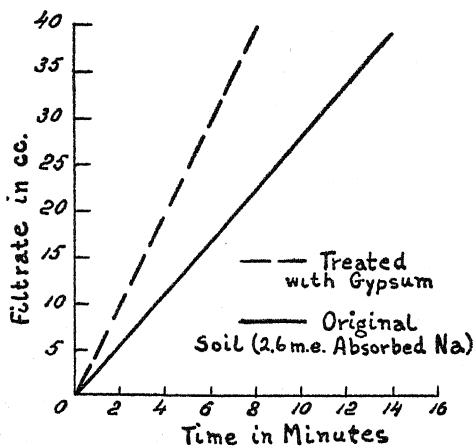


FIG. 3. INFLUENCE OF EXCHANGEABLE  $Na$  UPON THE FILTERABILITY OF EXTREMELY SOLONCHETIC SOIL, HORIZON A

ment, average samples of soil were taken from the pots, air-dried, ground in a mortar, and passed through a 0.5-mm. sieve. The capillarity and filterability of these samples were then determined.

The results, given in table 5 and figure 2, show that the 3 years' application of  $NaNO_3$ , which contributed comparatively small amounts of sodium to the



absorptive complex of the soil,<sup>1</sup> produced a considerable retardation in the rate of capillary movement of the water and a decrease in the filterability of the soil. The influence of exchangeable sodium on the physical properties of a natural solonetz soil are shown in table 6 and in figures 3 and 4, which give the corresponding data for horizon A and B of a strongly solonetzic soil from Chongar.

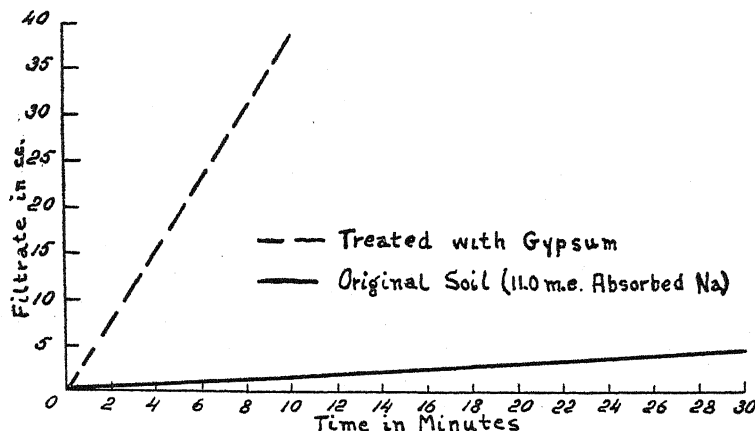


FIG. 4. INFLUENCE OF EXCHANGEABLE Na UPON THE FILTERABILITY OF EXTREMELY SOLONETZIC SOIL, HORIZON B

TABLE 6

*Influence of exchangeable Na in strongly solonetzic soil on its physical properties*

DESCRIPTION OF SAMPLE	CONTENT OF EXCHANGEABLE Na		CAPILLARY RISE		DISPERSABILITY <0.001 MM. PARTICLES IN PER CENT OF WEIGHT OF SAMPLE		SWELLING VOLUME OF 10 GM. OF SOIL IN WATER	
	M.e. per 100 gm. soil	Per cent of total exchangeable bases	Original soil	Treated with gypsum	Original soil	Treated with gypsum	Original soil	Treated with gypsum
			hours	hours			cc.	cc.
Extremely solonetzic soil from Chongar Peninsula:								
Horizon A (0-15 cm.) . . . . .	2.6	18.7	7	3	2.7	2.4	10.0	9.8
Horizon B <sub>1</sub> (15-49 cm.) . . . . .	11.0	45.0	288	36	26.6	4.4	24.0	13.7

These data show that in horizon B, as well as in horizon A, which contains comparatively small amounts of exchangeable sodium, the replacement of

<sup>1</sup> If we assume that all the sodium introduced with the saltpeter was absorbed, then the total amount of sodium taken up by the absorptive complex in 3 years is about 0.05 per cent of the weight of the soil, or about 4.5 per cent of the total exchangeable bases.

sodium by calcium as a result of treatment with gypsum leads to an increase of the filterable capacity of the soil and of the rate of capillary rise of water.

A comparison of the data in table 6 with those in table 4 indicates that the influence of exchangeable sodium on the physical properties of the soil, like that on plants, is greater in the case of a soil rich in organic substances (chernozem) than in the case of a soil poor in the organic substances (soils of the chestnut zone). It may be concluded, therefore, that under field conditions the deleterious effect of exchangeable sodium in the soil on the yield may also be evident in practice with a lower content in the soil than under conditions of pot culture.

These data also show that in the reclaiming of non-carbonate solonetz (in which there is no accumulation of soda) the chief object should be the improvement of the physical properties of the soil, because the content of exchangeable sodium in the soil, up to a certain very high limit, is not in itself a limiting factor in the development of plants. When choosing the dose of the meliorating substance (for instance, gypsum), it is also necessary to proceed from the peculiarities of its influence on the physical properties of the soil. As has been shown elsewhere (5), the physical properties of non-carbonate solonetz are essentially improved with doses of gypsum considerably smaller than would be expected from the computation of the content of exchangeable sodium in the soil.

In conclusion, let us consider the causes of destruction of plants with a very high content of exchangeable Na in the soil.

As has been indicated, soil reaction alone is not a sufficient explanation, for in the case of chernozem containing exchangeable Na to the amount of about 70 per cent of the total exchangeable bases, the reaction in the soil suspensions did not exceed pH 7.6 to 7.8.

Another possible cause of the destruction of plant life might be the accumulation of soda in the soil as the result of hydrolysis of the exchangeable sodium. To determine the possible importance of this factor, in the pot tests described in the foregoing two pots were included containing soil saturated 70 per cent with sodium, 15 per cent with calcium, and with the remaining 15 per cent not saturated with any base.<sup>2</sup> Thus this soil had a kind of "buffer" in the form of an unsaturated 15 per cent of bases which would prevent the accumulation of soda in the soil if any were formed. Both the oats and the wheat in those pots died soon after germination, however, and it is, therefore, difficult to explain the death of the plants by an accumulation of soda in the soil.

It is also very difficult to explain the destruction of the plants by the unfavorable physical properties of the soil, since soil 50 per cent saturated with sodium is very similar in these respects to that 70 per cent saturated; but in the first case the plants developed normally, whereas in the second case they died.

The destruction of the plants might be attributed to the immobilization of

<sup>2</sup> Schematically such a composition of exchangeable bases may occur in the case of solonetz which has been subjected to a process of solodization.

micro-elements in the soil (boron, manganese, etc.) occurring in the same way, as has already been pointed out, as in overlimed soils. But when micro-elements (Sommer-Lippman mixture) were introduced into the soil, the destruction of the plants was not prevented.

Finally, one of the causes of the death of plants when the soil contains a large amount of exchangeable sodium may be the lack of calcium to nourish the plants and, in general, the breaking down of the "calcium régime" in the soil, which, as is well known, acts as a regulator for a whole series of processes connected with plant nutrition.

Experimental verification of the importance of this factor is rather difficult, since introducing a source of calcium (e.g. gypsum) directly into the soil not only supplies the plants with calcium but also changes the character of the soil; on the other hand, supplying the plants with calcium by the method of isolated nutrition is also difficult, since, as is known from Domontowitsch's studies (1), calcium cannot be isolated from the other components of the nutrient mixture without injury to the plant.

Nevertheless, in the light of modern conceptions of the mobility of soil exchangeable bases, depending on the degree to which the absorptive complex is saturated by each of them, this last explanation of the destruction of plant life when there is a relatively high content of exchangeable sodium in the soil seems to be very plausible.

The following circumstances may serve as certain confirmation of the correctness of this explanation: Exchangeable magnesium, up to 50–60 per cent of the total exchangeable bases—as shown by the experiments of Drujinin, (2), O. K., and O. E. Kedrov-Sichman, (3) as well as by our experiments (4)—does not lead to a decrease of yield; whereas an increase of magnesium up to 70–80 per cent of the total exchangeable bases, in the experiments of Drujinin, brought about a sharp reduction of plant growth.

Apparently, in the case of magnesium, as in that of sodium, the cause of the suffering of the plants is the same: the difficulty in the nutrition of the plants with calcium, due to the depression of the hydrolysis of the exchangeable calcium under the influence of the predominance of another exchangeable cation in the soil absorbing complex.

It may be assumed that in the case of cations strongly hydrolyzed and easily dissociated by the soil particles, the depression of the mobility of the exchangeable calcium, in the presence of a predominance of those cations in the soil absorbing complex, is expressed more strongly than in the case of cations weakly hydrolyzed and weakly dissociated. The harmful action of the predominance in the soil of exchangeable sodium must, therefore, be evident earlier than with the predominance of the exchangeable magnesium.

#### SUMMARY

The influence of exchangeable sodium upon the physical properties of soils (the retardation of the capillary rise of water, the decrease in the filterability,

and the increase of dispersability and swelling) is very clearly defined even when there are only relatively small amounts of exchangeable Na in the soil (several per cent of the total exchangeable bases).

The influence of exchangeable sodium in chernozem soil on plant growth begins to be deleterious under the conditions imposed by pot tests only when it amounts to about 50 per cent of the total exchangeable bases. Death of the plants (oats and wheat) occurs when the exchangeable sodium in the soil increases to 60 to 70 per cent of the total exchangeable bases.

The unfavorable influence of exchangeable Na upon the physical properties of soil, as well as its harmfulness to plant growth, when there is a considerable quantity present in the soil, is more marked in soils rich in organic matter than in poorer soils.

The destruction of plant life in pot experiments when there is a large amount of exchangeable Na is difficult to explain (in the case of non-carbonate soils) by the alkaline reaction of the medium, by the accumulation of soda, or by the unfavorable physical properties of the soil. One of the possible causes of the destruction of plant life may be assumed to be the breaking down in the soil of the calcium régime, and in particular an insufficiency of calcium as one of the elements of plant nutrition.

The question of the limiting amounts of exchangeable sodium remaining harmless for the plant demands further elucidation in relation to carbonate soils. It may be assumed that in carbonate soils this limit is lower than in non-carbonate soils, because of the possibility, in the first case, of the formation of soda in the soil as a result of the exchange reaction between the exchangeable sodium and the carbonates of calcium and magnesium.

The chief object in the amelioration of non-carbonate solonchaks should be the improvement of the physical properties of the soil, because its richness in exchangeable sodium, up to a certain very high limit, is not in itself a circumstance disturbing the normal development of plants.

The data presented in this study illustrate the impossibility of obtaining a correct conception of the importance to the plant of the physical properties of soil on the basis of pot experiments.

#### REFERENCES

- (1) DOMONTOWITSCH, M. K. 1923 Ueber der Einfluss der Calciums auf die Entwicklung der Wurzeln bei Zea Mais. *Ergebnisse der Vegetations- und Laboratoriumsversuche* (Vorstand, D. N. Prianishnikow) 12: 187-199.
- (2) DRUJININ, D. W. 1933 Importance of magnesium in fertilizers and in the soil for plant yield. Collection of works *News in soil-fertilizing*, p. 31-55. Moscow [Russian].
- (3) KEDROV-SIECHMAN, O. K., and KEDROV-SIECHMAN, O. E. 1934 Influence of the composition of absorbed cations on the development of barley and clover. *Chemisation of Socialistic Agriculture* 12: 9-21 [Russian].
- (4) RATNER, E. I. 1933 Lime and gypsum on carbonate-free alkali soils. *Pedologie* 6: 464-475 [Russian].
- (5) RATNER, E. I. 1935 Use of natural magnesium silicates for the reclaiming of acid soil. *Mineral fertilizers and insecto-fungicides*. No. 2 [Russian].

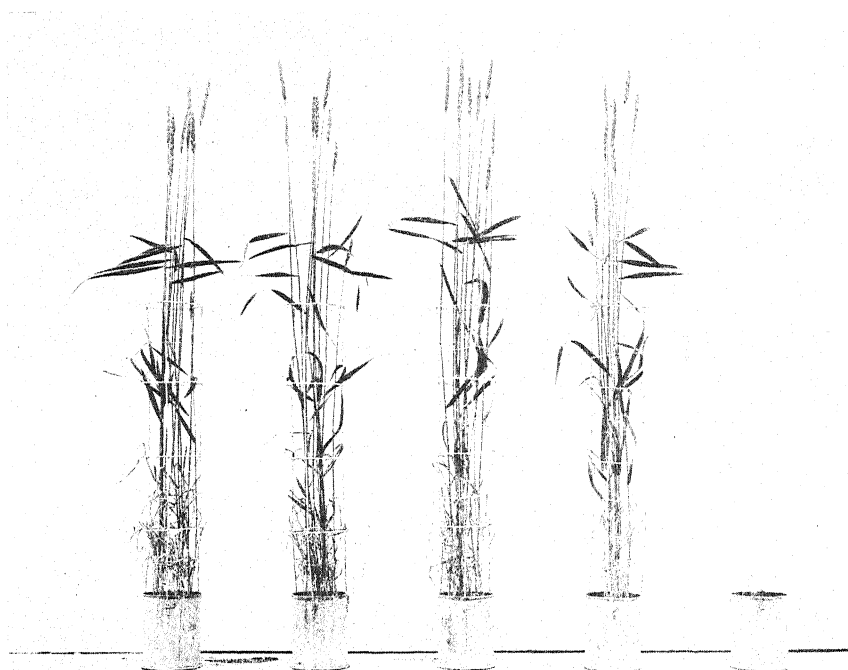
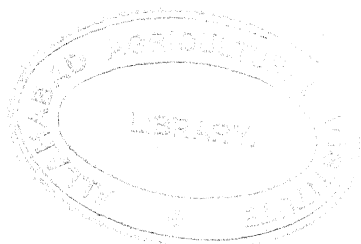
PLATE

## PLATE 1

THE INFLUENCE OF EXCHANGEABLE SODIUM IN CHERNOZEM SOIL UPON THE GROWTH OF  
SPRING WHEAT


Relation of exchangeable Ca to Na in the soil, left to right:  $\frac{100 \text{ per cent Ca}}{0 \text{ per cent Na}}$ ,

$\frac{85 \text{ per cent Ca}}{15 \text{ per cent Na}}$ ,  $\frac{70 \text{ per cent Ca}}{30 \text{ per cent Na}}$ ,  $\frac{50 \text{ per cent Ca}}{50 \text{ per cent Na}}$ ,  $\frac{30 \text{ per cent Ca}}{70 \text{ per cent Na}}$









## A SEDIMENTATION TUBE FOR ANALYZING WATER-STABLE SOIL AGGREGATES

RALPH C. COLE AND N. E. EDLEFSEN

*University of California*

Received for publication February 23, 1935

The tube described in this paper was designed to measure the size distribution of individual and compound particles that are present when a soil is slaked in water. The slaking of soil does not completely break it down to individual particles but permits many fine crumbs or aggregates to remain as such in the water. They are here defined as water-stable aggregates. Information on this state of aggregation is desirable in studying cultural treatments of field soils in relation to their effect on the rate of penetration of irrigation water.

Robinson (6) has suggested that the measurement of structure of soils be carried out as an extension of mechanical analysis. Tiulin (7) considers that the water-stable aggregates are the only true aggregates in the soil and that their measurement gives a clue to the productivity of a soil. Novak (5) prefers mechanical analysis of aggregates to a regular mechanical analysis after complete dispersion as a means of characterizing field soils. Baver and Rhodes (1) suggest aggregate analysis as a means of studying soil-structure relationships. Lutz (4) has offered it as a means of predicting the erosiveness of soils. Bouyoucos (2) has considered the size distribution of particles when a soil is slaked in water as the "ultimate natural structure" of the soil.

The common methods of making mechanical analysis of soils are to separate the coarser particles into various size grades by means of sieves and to separate the finer particles by means of sedimentation or elutriation methods. Bouyoucos (2), however, suggested the use of the hydrometer method for measurements of "ultimate natural structure," but later (3) he concluded that this method is not suitable for measuring particles larger than the upper limit of silt (diameter 0.05 mm).

It is desirable to have a method whereby the whole range of sedimentation velocities can be measured instead of using wet sieving for coarser particles and elutriation or sedimentation for finer particles. The use of wet sieving seems particularly objectionable because the mechanical action necessary in the sieving operation has a dispersing effect on the compound particles, thus giving an abnormally high per cent of fine particles. Evidence of the dispersing action caused by sieving is given in table 1.

The wet sieving was carried on through a series of sieves having the following

openings: 0.991 mm., 0.495 mm., 0.246 mm., 0.104 mm., and 0.053 mm. A 50-gm. sample of soil was placed in the coarsest sieve, which was then put in a shallow pan of distilled water, to a sufficient depth to cover all the soil, and allowed to slake for at least 2 hours. In no soil used by the authors did the state of aggregation of the sample change after slaking for greater lengths of time. Bouyoucos (2) has also found 2 hours to be sufficient for breaking down all the aggregates into their water-stable state, whereas Tiulin (7) found 30 minutes to be sufficient for this slaking for wet-sieving analysis. Novak (5) found 2 hours to be sufficient, except for very ferruginous soils, which required 24 hours to slake down to their water-stable state. After the slaking period, the sieve was raised, drained, and dipped into the pan 50 times, the number of times being arbitrary, except that preliminary tests showed very little additional soil passed through the sieve when a greater number of dippings were made, a fact indicating that most of the smaller material had passed through. The material remaining on the sieve was dried in an oven at 105°C. and weighed. The material passing through was transferred to the next sieve, and the same procedure was followed for the whole series of sieves.

TABLE 1

*Analysis of three different samples of Yolo loam by wet sieving and sedimentation methods*

Results are expressed as per cent of total sample composed of particles with diameters of less than 0.053 mm.

METHOD	1	2	3
Wet sieving .....	43.12	40.96	50.37
Sedimentation.....	18.92	19.60	28.06

The percentage of material (table 1) small enough to pass through the sieve having 0.053-mm. openings is much greater than the percentage of material determined by means of sedimentation and calculation, assuming Stoke's Law, and a particle density of 2.65. This density is admittedly too high for most soil aggregates. If a lower value had been used in this calculation the percentage by sedimentation (table 1) would have been still lower. The differences are so great that they can be explained only on the basis of a mechanical breaking down of the water-stable aggregates in the process of sieving. Evidently the apparatus for analyzing these aggregates must be one that will disturb them as little as possible while determining their size distribution.

The apparatus designed to measure the size distribution of particles when slaked in water, without appreciably breaking up the particles, consists of a brass tube (fig. 1) 30 inches long, inside of which is another brass tube of the same length machined to fit snugly. The inside tube is cut into sections 2 inches long with machined ends, so that there is a close fit at the joints of the various segments. Caps are fitted to screw on both ends of the outside tube so that the segments are held tightly in place. The bottom cap is flat and has

several holes closed with screws, which may be removed for the purpose of drainage. The top cap is hollowed out slightly, and is fitted with a petcock so that the tube can be completely filled with water. There are also a number of holes in this cap closed with screws which may be used for drainage.

The procedure in making a determination is as follows: The bottom cap, with all holes closed, is screwed on the outer tube. The inner tube is put in place and nearly filled with distilled water. Sufficient soil is then added to make 54 gm. of oven-dry soil (2 per cent suspension) and allowed to slake for at least 2 hours. The tube is filled level full of water, the temperature recorded, the top cap screwed on, and the hollow portion of the cap filled with water through the petcock in the top. The tube thus assembled and filled is mounted

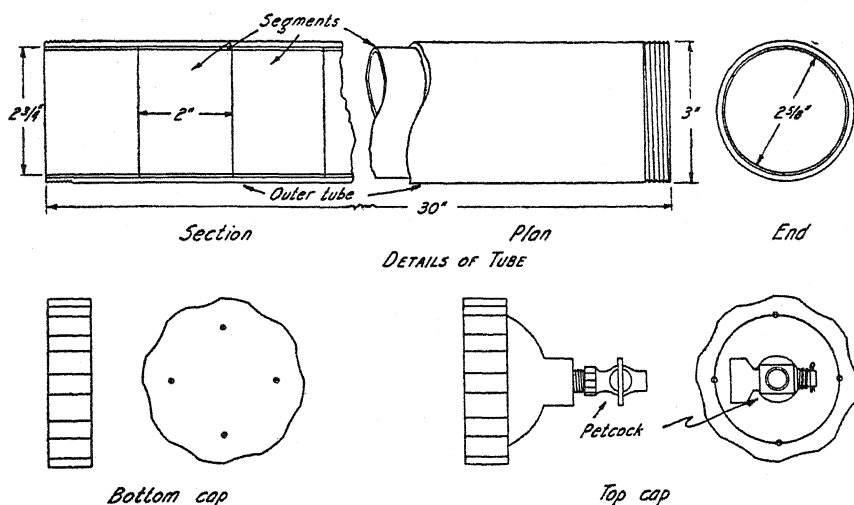


FIG. 1. DIAGRAM OF SEDIMENTATION TUBE

on a wheel, which is free to turn, and is rotated in a manner which, as explained later, produces a fairly uniform distribution of the particles in suspension.

After mixing is complete, the tube is brought to a vertical position, the settling is allowed to take place parallel to the axis of the tube for a designated time, and then the tube is quickly turned to a horizontal position and allowed to stand 10 to 12 hours so that the particles will settle perpendicular to its axis on the walls of the segments. The water is then drained off by removing the screws from the upper portion of the tube first and allowing the water to run out drop by drop. After draining, which requires from 10 to 12 hours, the tube is dismounted, the inner tube is taken out, the material collected on each segment carefully washed into beakers, the water evaporated, and the residue weighed. Each 2-inch segment is considered as a unit, and the average settling velocity for each is obtained by dividing the time into the distance from the top of the column to the center of each segment.

According to observations on glass tubes, if the tube is completely filled with soil and water, so that there are no air bubbles to stir up the suspension, particles do not materially change their position when the tube is rotated from the vertical to the horizontal.

No air bubbles being present, longer intervals between rotations are necessary at the beginning of the mixing process to get the finer particles distributed throughout the tube. The intervals between rotations are successively shortened until a fairly uniform distribution of all particles is obtained. The plan adopted (method II, table 2) is to turn the tube top down for 1 minute, then invert it for 50 seconds, again for 40 seconds, then 30, then 20, 10, 9, 8,

TABLE 2

*Distribution of soil throughout the tube on each segment at zero settling time as obtained by the two methods of mixing explained in the text*

(a) and (b) are separate tests under each method

SEGMENT	METHOD I		METHOD II	
	(a)	(b)	(a)	(b)
	gm.	gm.	gm.	gm.
1	8.46	8.11	5.29	3.75
2	3.89	4.76	2.65	3.26
3	3.97	3.83	2.92	3.34
4	3.69	3.60	3.08	3.38
5	3.43	3.27	3.11	3.05
6	3.25	3.20	3.13	3.25
7	2.91	3.20	3.16	3.19
8	2.67	3.06	2.95	4.36
9	2.90	2.81	2.80	3.76
10	2.90	2.65	2.99	3.43
11	3.06	2.85	2.93	3.41
12	2.65	2.88	3.57	3.22
13	2.53	2.48	3.77	3.46
14	2.59	2.15	4.97	3.41
15	2.20	1.98	3.59	3.75

7, 6, 5, 4, 3, 2, and 1 seconds. This method is compared with a method using 30 rotations with uniform intervals between each, as commonly used in mixing for mechanical analysis (method I, table 2). The data indicate that a more uniform distribution of particles is obtained by mixing by method II than by method I.

A number of tests have shown that the aggregates are so stable that the agitation necessary to obtain even distribution, as has been indicated, has a negligible dispersing effect. This seems to be in accord with observations made by Bouyoucos (2).

A number of replications at three different settling periods were made on a sample of Sacramento adobe clay. Some of the data are presented in figure 2.

All of the settling velocities have been corrected to 20°C. using Stoke's formula  $v = \frac{Kr^2}{\eta}$ , which accounts for replicates not always occurring at the same value for  $v$ . The replicates for any settling period give good checks. The data

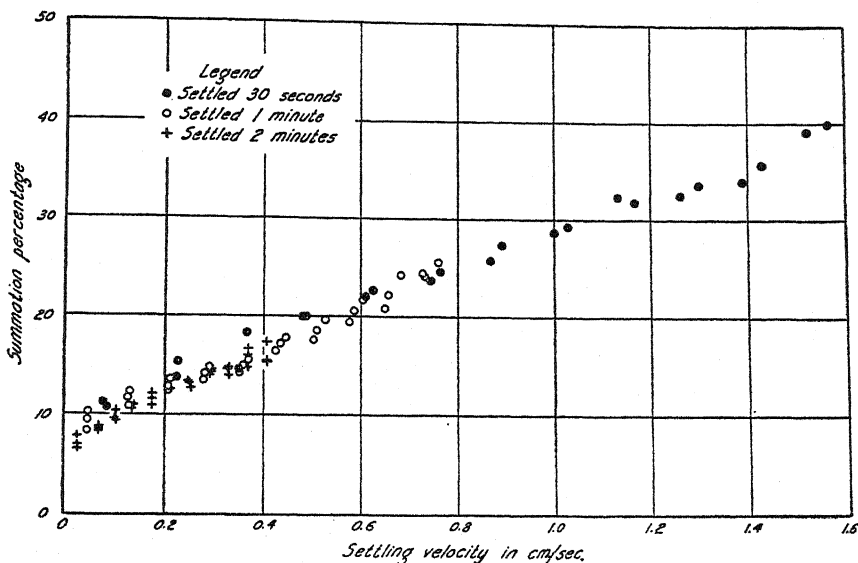


FIG. 2. PERCENTAGE OF PARTICLES HAVING SETTLING VELOCITIES EQUAL TO OR LESS THAN VALUES INDICATED ON THE GRAPH  
Settling velocities corrected to temperature of 20°C.

TABLE 3

*Percentages of dispersed soil having settling velocities equal to or less than definite values, as measured by the tube and pipette methods*

MAXIMUM SETTLING VELOCITIES IN CM. PER SECOND	SACRAMENTO ADOBE CLAY		YOLO LOAM	
	Tube	Pipette	Tube	Pipette
0.25	92.2	93.1	56.8	56.8
0.083	89.3	91.2	49.9	50.2
0.050	88.3	89.7	46.0	45.8
0.025	87.1	86.2	42.0	38.7
0.0125	83.1	83.2	30.2	33.1
0.0083	83.6	80.7	30.0	31.2
0.0042	76.5	72.8	24.1	26.2

further show that the percentage of material having settling velocities equal to or less than any definite amount is practically the same for all settling periods used. The fact that the determinations give good checks for the same maximum settling velocities, whether replicated at the same settling period or determined at a different depth using different settling periods, not only

emphasizes the validity of this method for making accurate measurements of the amount of material in suspension, but supports the soundness of the "mean effective diameter" (mean settling velocity) concept. A mean settling velocity of any group of particles apparently remains constant throughout the course of sedimentation. With the 30-second settling period, it seems that the percentage of particles having low settling velocities is a little higher than for the other settling periods. This indicates that the turbulent effect of the mixing of the sample was not completely dissipated and was greater on the particles of low settling velocities. Shorter settling periods than this should probably not be used.

A further indication of the accuracy of the tube is shown by analyzing dispersed samples of Sacramento adobe clay and Yolo loam, using the tube as compared to the pipette. The samples were dispersed with an electrically driven "egg beater" for 10 minutes and sodium oxalate was added as a dispersing agent. In both instances the pretreatments were alike, so that they should serve as a means of comparing the two methods.

The results (table 3) with the tube agree well with those of the pipette over the range of settling velocities where both methods can be used. The authors do not propose this tube as a substitute for the pipette for mechanical analysis of dispersed soils. With the pipette method, however, it is difficult to measure material in suspension having settling velocities greater than 0.25 to 0.30 cm. per second. With the tube herein described, material in suspension having settling velocities of 1.6 cm. per second can be measured; and by lengthening the tube, greater settling velocities can be studied. Its reasonable accuracy, together with the possibility of its use to investigate the entire range of settling velocities of water-stable aggregates, indicates its usefulness in this field.

In recording the data settling velocities are used here rather than the particle size as calculated by Stoke's Law, because of the presence in such suspensions of both individual and aggregated particles the densities of which may be considerably different. If a crumb and an individual particle were found to have the same settling velocity, the crumb having the lower density would necessarily have the larger mean diameter. For example, let us assume a water stable aggregate to have an apparent density of 1.50. This would mean that the aggregate would have 43.4 per cent pore space, if the density of individual particles is assumed to be 2.65. Let us further assume that in the settling of a water-stable aggregate the water within the pore space is carried down with the particle. The density of the crumb in the form in which it settles would then be  $1.50 + 0.434$ , or 1.934. Applying Stoke's Law and calculating the mean diameter of the crumb, which will have the same settling velocity as an individual particle the density of which is assumed to be 2.65, we find the ratio of the diameters will be 1.33 to 1.00.

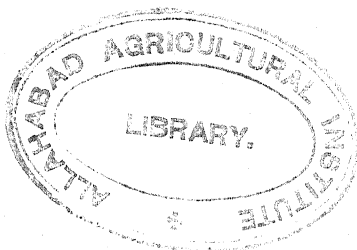
A sedimentation tube is described in which settling velocities as great as 1.6

cm. per second can be satisfactorily measured. This is higher than the maximum settling velocities usually measured by sedimentation methods.

Determinations on dispersed samples check well with the pipette over the range of settling velocities covered by both methods.

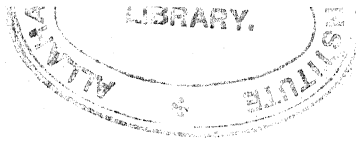
#### REFERENCES

- (1) BAYER, L. D., AND RHODES, H. F. 1932 Aggregate analysis as an aid in the study of soil structure relationships. *Jour. Amer. Soc. Agron.* 24: 920-930.
- (2) BOUYOUCOS, G. J. 1929 The ultimate natural structure of soils. *Soil Sci.* 28: 27-37.
- (3) BOUYOUCOS, G. J. 1934 A comparison between the pipette method and the hydrometer method of mechanical analysis of soils. *Soil Sci.* 38: 335-346.
- (4) LUTZ, J. FULTON 1934 The physico-chemical properties of soils affecting soil erosion. *Missouri Agr. Exp. Sta. Res. Bul.* 212.
- (5) NOVAK, VACLAR 1932 Contributions to the study of soil structure I. *Bul. Czechoslovak Acad. Agr.* 8: 756-759; [German] 759-761.
- (6) ROBINSON, G. W. 1934 The work of Commission I (Soil Physics). *Soil Res.* 4: 125-127.
- (7) TIULIN, A. TH. 1928 Same questions on soil structure. II. Aggregate analysis as a help method for determination of the real soil structure. Reprinted from "Results of investigations of the Perm (U. S. S. R.) Agricultural Experiment Station, Division of Agricultural Chemistry," No. 2.









# A METHOD FOR MAKING MECHANICAL ANALYSIS OF THE ULTIMATE NATURAL STRUCTURE OF SOILS<sup>1</sup>

GEORGE JOHN BOUYOUCOS

*Michigan Agricultural Experiment Station*

Received for publication March 25, 1935

In previous works (1, 2, 3), it has been shown that when soils in the dry and field condition are placed in an excess of water, they disintegrate or slake into particles or granules of various sizes. These particles or granules seem to be in an ultimate natural size and stable condition, because according to the hydrometer method (3) they do not get smaller upon standing in water for an indefinite length of time or upon gentle shaking. Indeed, allowing the soils to stay in water for 5 days or shaking them by hand in a liter cylinder from 6 to 30 times resulted in little change in particle size. It would take very long and vigorous shaking or the application of a considerable amount of energy to break up these particles or granules from their natural, stable condition.

A measurement of the ultimate natural structure of soils may have a very significant practical value in such fundamental soil properties as erosiveness, percolation, and tilth.

Since slaking appears to be a fundamental phenomenon and since the slaked product is considered to represent the ultimate natural structure of soils, it has seemed advisable to work out a method for measuring this structural condition. An attempt was previously made to make a mechanical analysis of this structure by the hydrometer method (3). Unfortunately, however, this method cannot measure particles or aggregates larger than about 0.12 mm. in diameter and consequently it does not give a complete analysis and distribution curve of all the particles and aggregates in the soil.

It is the purpose of this paper, therefore, to present the method developed for making a mechanical analysis of the ultimate natural structure of soils, and to give results obtained by the use of the method.

## METHOD AND PROCEDURE

The method finally adopted for making a mechanical analysis of the ultimate natural structure of soils is a combination of the sieve method and the hydrometer method. In the sieve method 6 different sieves were employed; namely, 10, 20, 40, 60, 80, and 100 mesh. The procedure consisted of filling a pan 2 inches deep and 8 inches wide with distilled water and placing sieve No. 10 into this pan. Then on this sieve is placed 50 gm. (on oven-dry basis)

<sup>1</sup> Journal Article No. 214 (n.s.) from the Michigan Agricultural Experiment Station.

*Mechanical analysis of the ultimate natural structure of soils and their ultimate mechanical composition*

SIEVE NO.	DIAMETER OF SIEVE HOLES	SOIL RETAINED BY SIEVES AFTER SLAKING AND GENTLE STIRRING	SOIL RETAINED BY SIEVES AFTER COMPLETE DISPERSION	CLAY 0.005-.000 MM.	FINE CLAY 0.002-.000 MM.
<i>Davidson clay loam (30 inches)</i>					
	mm.	per cent	per cent	per cent	per cent
10	2.00	13.5	0.00	55.2	49.2
20	0.84	31.8	0.04		
40	0.42	32.2	1.00		
60	0.25	8.0	0.30		
80	0.18	4.0	1.16		
100	0.15	2.0	0.86		
Total .....		91.5	3.36		
<i>Irredel loam B</i>					
10	2.00	6.1	0.0	57.0	53.0
20	0.84	21.6	1.4		
40	0.42	40.3	1.2		
60	0.25	7.3	1.1		
80	0.18	5.7	1.3		
100	0.15	4.0	1.3		
Total.....		84.5	6.3		
<i>Susquehanna clay loam (24 inches)</i>					
10	2.00	0.4	0.00	45.4	42.2
20	0.84	3.2	0.26		
40	0.42	21.2	0.06		
60	0.25	15.5	0.08		
80	0.18	22.0	0.44		
100	0.15	6.0	8.20		
Total.....		68.3	9.04		
<i>McKenzie clay A<sub>2</sub></i>					
10	2.00	0.4	0.00	68.4	67.4
20	0.84	6.0	0.10		
40	0.42	15.8	0.20		
60	0.25	8.4	0.44		
80	0.18	4.0	0.60		
100	0.15	4.4	0.40		
Total.....		39.0	1.74		
<i>Ontonagon clay C</i>					
10	2.00	3.8	0.00	84.6	78.6
20	0.84	13.7	0.00		
40	0.42	28.8	0.08		
60	0.25	14.8	0.20		
80	0.18	7.6	0.08		
100	0.15	3.8	0.06		
Total.....		72.5	0.42		

TABLE 1—*Concluded*

SIEVE NO.	DIAMETER OF SIEVE HOLES	SOIL RETAINED BY SIEVES AFTER SLAKING AND GENTLE STIRRING	SOIL RETAINED BY SIEVES AFTER COMPLETE DISPERSION	CLAY 0.005-.000 MM.	FINE CLAY 0.002-.000 MM.
<i>Pease clay 60 inches</i>					
10	2.00	0.0	0.00	45.4	43.4
20	0.84	0.2	0.14		
40	0.42	2.0	0.12		
60	0.25	6.2	0.36		
80	0.18	6.6	0.62		
100	0.15	4.8	0.76		
Total.....		19.8	2.00		
<i>Fargo clay loam 0-6 inches</i>					
10	2.00	19.0	0.00	52.0	44.0
20	0.84	10.4	0.66		
40	0.42	24.2	0.84		
60	0.25	16.8	1.10		
80	0.18	7.2	1.50		
100	0.15	3.8	1.00		
Total.....		81.4			
<i>Zanesville silt loam surface</i>					
10	2.00	1.6	0.00	26.0	22.0
20	0.84	7.8	0.42		
40	0.42	17.0	0.44		
60	0.25	15.2	0.36		
80	0.18	8.8	0.02		
100	0.15	7.8	0.16		
Total.....		58.2	0.58		
<i>Fine sandy loam surface</i>					
10	2.00	1.9	1.60	6.6	5.2
20	0.84	1.5	0.80		
40	0.42	1.7	1.10		
60	0.25	9.0	11.00		
80	0.18	23.4	27.00		
100	0.15	22.0	19.60		
Total.....		59.5	61.00		

of lump soil as it comes from the field and after air-drying but not being ground or broken up in any way. The soil is allowed to soak and slake for about 24 hours. Then the sieve is gently shaken in the water, and the soil particles or aggregates smaller than the holes of this sieve go through, and

those larger than the holes of the sieve are retained. Then sieve No. 20 is placed in a second empty pan, the contents of the first pan are gently washed into it, and again the sieve is gently shaken in the water until there is a separation between the material that will go through No. 20 sieve and that which will not go through it. This process is repeated separately and carefully for each sieve. The sieves are then put in the oven, and, after drying, their contents are weighed carefully. In order to prevent loss of material, a sheet of paper is placed under each sieve during drying. All the soil material that went through the finest sieve used, 100 mesh, was saved in a large beaker and was finally mixed with all the material that was retained by the various sieves, and the mixture was dispersed and mechanically analyzed by the hydrometer method. At the conclusion of the final hydrometer reading the soil, now in a completely dispersed state, was again passed through each of the 6 sieves in order to obtain a direct comparison between that amount of the soil material retained by each sieve after slaking only and after complete dispersion, and thus to ascertain the amounts of sand that might have been counted as granules.

The method as described has worked well in obtaining a mechanical composition of the ultimate natural structure of soils. By shaking the sieves in the usual manner under water a satisfactory separation of the particles seems to be attained. At the present time, the sieve method is probably the most practical method for measuring the ultimate natural structure of soils.

The results obtained by the sieve and hydrometer methods are presented in table 1.

An examination of the results in table 1 reveals at once the striking fact that the ultimate natural structure varies considerably with the different soils. It will be noted that the amount of the slaked soil retained by the sieves ranges from 19.8 per cent in the case of Pease clay to 91.5 per cent in the case of Davidson clay loam. In the majority of soils the amount of aggregates retained by the sieves is high, varying from about 60 per cent to 90 per cent. Since the openings of the sieves range from 2.0 to 0.15 mm. in size, it is readily seen that the ultimate natural structure tends to be relatively coarse in the majority of the soils. The results reveal the fact that most of the aggregates in any one soil range in size from about 0.84 to about 0.25 mm.

#### SUMMARY

When lumps of air-dry soils are placed in an excess of water, they slake or disintegrate into particles or granules of various sizes.

These slaked particles or granules are considered to represent the ultimate natural structure of soils, because they appear to be stable and they require the application of external energy and dispersing agents to break them up further.

An attempt was made to work out a method for making mechanical analysis of this ultimate natural structure of soils. A combination of the sieve method and the hydrometer method was finally adopted for this purpose.

The results obtained show that the ultimate natural structure varies considerably with the different soils but is distinct for each soil. As a general rule the ultimate natural structure of most soils seems to be coarse, ranging in size from about 2.0 to 0.15 mm. Many soils have more than 90 per cent of their particles or aggregates in this range.

#### REFERENCES

- (1) BOUYOUCOS, G. J. 1924 The influence of water on soil granulation. *Soil Sci.* 18: 103-109.
- (2) BOUYOUCOS, G. J. 1927 Texture and structure of soils as influenced by chemical agents. *Jour. Amer. Soc. Agron.* 19: 788-797.
- (3) BOUYOUCOS, G. J. 1929 The ultimate natural structure of soils. *Soil. Sci.* 28: 27-37.



# THE RÔLE OF PLANT CONSTITUENTS IN THE PRESERVATION OF NITROGEN IN THE SOIL<sup>1</sup>

SELMAN A. WAKSMAN AND I. J. HUTCHINGS

*New Jersey Agricultural Experiment Station*

Received for publication April 12, 1935

Every system which has for its aim the building up of the humus content of the soil, whether preliminary decomposition of the plant and animal residues is carried out in composts or directly in soil, involves a knowledge of the transformation of the three major groups of plant constituents; namely, the carbohydrates, largely the cellulose and hemicelluloses, the lignins and the proteins. Since the process of humus formation consists in the decomposition of some of the constituents of the plant and animal residues and in the preservation and accumulation of others, as a result of the activities of microorganisms, an understanding of the physiology of these organisms is essential. Among the elements most important in plant nutrition that are conserved in the soil by the presence of humus, nitrogen occupies the leading place.

In the absence of humus, nitrogen does not accumulate in the soil and, even when added to the soil, if it is not used rapidly by the growing crop, it tends to disappear by a variety of processes. When fresh plant residues are allowed to decompose, both in soils and in composts, the nitrogen present in these residues, or added to them, or made available through biological activities upon the soil humus is transformed by the agency of microorganisms into complex organic substances; these form one of the most important groups of humus constituents. The plant residues thus play a significant function in the preservation of the nitrogen, both in the compost and in the soil.

Of the various plant constituents, the carbohydrates and the lignins are most important, both in the process of humus formation and of nitrogen conservation. The carbohydrates disappear rapidly in the process of decomposition of the plant residues; the rate of their disappearance depends upon their specific nature, upon the amount of nitrogen available for the growth of the microorganisms capable of attacking them, and upon the conditions favoring the activities of various specific groups of fungi, bacteria, actinomyces, and invertebrate animals. These organisms make use of the energy liberated in the decomposition of the carbohydrates and synthesize considerable cell substance, with the result that mineralized nitrogen is transformed into microbial cell

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, New Brunswick, N. J., department of soil chemistry and bacteriology.

substance. In the case of pure cultures of fungi, it was found (4) that as much as 1 part of nitrogen is consumed for every 30 parts of cellulose decomposed; with mixed cultures of bacteria and fungi this ratio is considerably wider. The function of carbohydrates in the preservation of mineralized nitrogen in soils or in composts thus consists in supplying available energy to the microorganisms, which are able to convert this nitrogen into organic forms.

Lignins, however, play a totally different rôle in the process of nitrogen conservation. They exert a specific effect upon two of the most important forms of nitrogen that find their way into the soil; namely, ammonia and protein: the first is absorbed by the lignin and is held in an absorbed condition until utilized by the plants or microorganisms or oxidized by specific bacteria to nitrate; the proteins combine with lignin, in a physical or chemical manner, giving complexes which are highly resistant to decomposition and which form an essential group of humus constituents (6).

The three most important forms of nitrogen which find their way into the soil; namely, protein, ammonia, and nitrate, are thus affected by the various plant constituents in a variety of processes: 1. Proteins added to the soil, or formed there as a result of microbial action, can either be decomposed, giving rise to ammonia, or, in the presence of sufficient quantities of lignin, are absorbed by the latter to give rise to ligno-protein complexes. The relative concentrations of protein decomposed or absorbed depends on the relative amounts of protein and lignin and upon the conditions of decomposition. 2. Ammonia exists in normal soils in a free state only in very limited concentrations; however, since it is the final product of protein decomposition, it is constantly produced in the soil. It usually does not remain there as such, but is either assimilated in the presence of carbohydrates by the microorganisms and converted into microbial proteins, absorbed by the organic and inorganic soil complexes, or oxidized to nitrates, or assimilated by higher plants, or volatilized and lost to the atmosphere, especially in poorly buffered non-acid soils. 3. The final product of nitrogen transformation in soil, namely, nitrate, can also either be assimilated by microorganisms, in the presence of carbohydrates, or utilized by higher plants, or washed out in the drainage water, or reduced to gaseous forms of nitrogen under anaerobic conditions.

An extensive literature has accumulated on the specific effect of carbohydrate-rich plant residues, especially cereal straw, upon the removal of available nitrogen from the soil by the microorganisms attacking the carbohydrates. In some cases, this effect has even been ascribed (1) to some specific toxic action of the plant materials. It has been shown (2), however, that this effect can usually be overcome by the addition of available nitrogen. No attempt will be made to review this literature. The experiments reported here are limited to a study of the effect of plant material as a whole, in the form of cereal straw, and especially of its carbohydrate (cellulose) and lignin constituents upon the preservation of nitrogen in the soil. Some of the results presented here have already been presented in a preliminary form elsewhere (5).



## EXPERIMENTAL

In order to eliminate the interfering action of soil organic matter and at the same time to produce conditions similar to those which prevail in an ordinary soil, sand was selected as the medium for the study of nitrogen transformation by microorganisms. One-kilogram portions of washed sand were placed in a series of small pots. Enough water was added to make conditions favorable for the activities of aerobic microorganisms. All pots received, at the beginning of the experiment, 0.5 gm. KCl, 0.5 gm.  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.1 gm.  $\text{FeSO}_4$ , and 2 gm.  $\text{CaCO}_3$ . Two months later, 0.5-gm. portions of  $\text{K}_2\text{HPO}_4$  were added to each pot; this was repeated again after three months, when 1.0-gm. portions were added.

The pots were divided into several groups. Some received, at definite intervals, varying amounts of cellulose, in the form of ground filter paper; others received lignin (alkali lignin from straw, unless otherwise stated); and still others received ground cereal straw. The nitrogen was used in the form of di-ammonium phosphate or casein; the latter was added as a neutralized alkali solution. All the pots were inoculated with an infusion of fresh soil and incubated at 25–28°C. At definite intervals, the pots were weighed and the moisture content was adjusted, after a thorough mixing of the contents. In the first two analyses, only the ammonia and cellulose contents were determined; after 2, 6, and 11 months' incubation, complete analyses were made of the total residual organic matter, of its different chemical constituents, and of the various forms of nitrogen present. During the first 6-month period, the various pots received 150 gm. of cellulose or straw, 25 gm. of lignin, 18 to 24 gm. of casein, and 4.5 to 7.5 gm. of  $(\text{NH}_4)_2\text{HPO}_4$ . At the end of 6 months, 25 gm. of cellulose was added to the corresponding pots and the whole series incubated again for another 5 months. The moisture content was kept at optimum by frequent additions of water when necessary.

The influence of alkali lignin upon the preservation of the two forms of nitrogen is brought out in table 1. When a neutral ammonium salt was added to sand and kept in closed containers and at optimum moisture, whereby losses from drainage and from excessive volatilization were prevented, as much as 27.6 to 44 per cent of the nitrogen was lost. The reaction of the medium was close to neutrality. Active nitrate formation began to take place within two months. Since practically no organic nitrogen was synthesized in these pots, the sum of ammonia and nitrate may be looked upon as representing the total nitrogen present. When lignin was also added, however, its mere contact with the ammonium salt was sufficient to reduce the losses of nitrogen to less than 10 per cent or stop it completely. Some of the nitrogen was at first changed to an organic form, as shown by an increase in organic matter content and in organic nitrogen; later, some of the lignin began to undergo decomposition. No nitrogen was lost, however, in this process. The reaction of the medium in the presence of lignin was changed to slightly acid, although this acidity had no injurious effect upon the process of nitrate formation.

When protein was added to the sand medium, it underwent rapid decomposition and ammonia was set free; largely because of a lack of sufficient buffer-

TABLE 1

*Influence of alkali lignin on the preservation of ammonia and protein nitrogen in a sand medium*

All data reported per total 1,000 gm. of sand medium

DATE OF ADDITION OR ANALYSIS	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	CASEIN	LIGNIN	ORGANIC MATTER LEFT (C x 1.724)	pH	NITROGEN FOUND			NITROGEN LOST, PER CENT OF TOTAL ADDED
						NH <sub>3</sub> -N	NO <sub>3</sub> -N	Total	
	mgm. N	mgm. N	gm.	gm.		mgm.	mgm.	mgm.	
3/ 7/34	318	.....	..	.....	...	...	...	.....	....
3/26/34	318*	.....	..	.....	...	230	...	230	27.6
4/17/34	318*	.....	..	.....	...	412	...	412	35.2
5/24/34	...	.....	..	0.05	...	531	35	566	40.6
9/18/34	...	.....	..	Trace	6.6	438	102	540	43.6
2/11/35	954†	.....	..	0.58	6.6	372	186	558	41.5
3/ 7/34	318	.....	5	.....	...	...	...	.....	....
3/26/34	318*	.....	5*	.....	...	262	...	262	17.6
4/17/34	...	.....	5*	.....	...	456	...	456	28.3
5/ 4/34	318	.....	10	.....	6.3	...	...	.....	....
5/24/34	...	.....	..	25.29	...	669	73	864	9.4
9/18/34	...	.....	..	28.22	6.4	493	97	902	5.4
2/11/35	954†	.....	25‡	21.86	6.4	473	118	990	0
3/ 7/34	...	408	..	.....	...	...	...	.....	....
3/26/34	...	408*	..	.....	...	94	...	94	77.0
4/17/34	...	816*	..	.....	...	116	...	116	85.8
5/24/34	...	.....	..	0.94	7.4	67	0	154	87.4
6/14-7/27	...	816	..	.....	...	...	...	.....	....
9/18/34	...	.....	..	1.40	7.0	28	87	356	85.5
2/11/35	...	2,448†	..	1.38	6.7	16	118	298	88.0
3/ 7/34	...	408	5	.....	...	...	...	.....	....
3/26/34	...	408*	5*	.....	...	138§	...	.....	66.2§
4/17/34	...	816*	15*	.....	...	232§	...	.....	71.6§
5/24/34	...	.....	..	27.15	7.1	295	46	940	42.4
6/14-7/27	...	816	..	.....	...	...	...	.....	....
9/18/34	...	.....	..	30.91	5.2	193	132	1,130	53.8
2/11/35	...	2,448†	25‡	26.54	5.4	315	288	1,370	44.0

\* Added after analysis was made.

† Total nitrogen added per pot.

‡ Total lignin added.

§ No total nitrogen determinations made; the ammonia represents only a part of the nitrogen, since some of the casein was not decomposed and remained as ligno-protein complex; hence, the losses here are no doubt much smaller than could be calculated from the ammonia figures alone.

ing material, much of the ammonia was volatilized, to the extent of 77 to 88 per cent of the total nitrogen added. The reaction of the medium was only

slightly alkaline (pH 7.0–8.4); with the accumulation of nitrates, the reaction became slightly acid. Only a small amount of nitrogen was conserved in the sand medium, for the following reasons: because of the accumulation of free ammonia, nitrate formation by bacteria was considerably delayed; the synthesis of cell substance by the microorganisms decomposing the protein was very small, since the latter was the only source of available energy.

The addition of lignin to the pots receiving casein reduced the loss of the nitrogen. This was brought about, on the one hand, by a delay in the decomposition of the protein, as shown by the large amount of organic nitrogen in the pots containing the lignin; on the other hand, the presence of lignin resulted in binding some of the ammonia, as shown by the fact that considerably larger amounts of this form of nitrogen were found in the pots containing lignin, even after 11 months' incubation. The losses of nitrogen added to the sand medium in the form of casein were reduced, in the presence of lignin, to about one half. Since the ratio of lignin to protein was narrow, about 2 to 1, the conservation of the nitrogen was not complete. It was found in other experi-

TABLE 2

*Influence of acid lignin\* upon the preservation of ammonia and protein nitrogen in a sand medium*

SOURCE OF NITROGEN	AMOUNT OF NITROGEN ADDED	NITROGEN FOUND			NITROGEN LOST, PER CENT OF TOTAL ADDED
		NH <sub>3</sub> -N	NO <sub>3</sub> -N	Total	
	mgm.	mgm.	mgm.	mgm.	
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> .....	1,272	508	103	1,111	13.4
Casein.....	1,632	62	127	883	45.9

\* 20 gm. per pot; period of incubation, 95 days.

ments (6) that when about four parts of lignin are present for each part of protein, the losses of nitrogen can be stopped almost completely.

The specific effect of lignin in preventing the losses of nitrogen from a sand medium was again determined by using acid lignin prepared from rye straw. The results obtained (table 2) fully confirm the previous observations on the effect of alkali lignin. In the case of the ammonia nitrogen, there was again practically no loss, whereas in the case of the protein, the losses were reduced by the presence of the lignin.

The next series deals with the effect of cellulose in preserving nitrogen in a sand medium. The results obtained from this experiment are quite different from those found with the lignin. The nitrogen in the form of the ammonium salt was added in quantities just slightly in excess of the need of the fungi and bacteria decomposing the amount of cellulose added to the pots, as shown by the fact that some nitrogen was always present as ammonia; most of the nitrogen, however, was consumed and transformed into organic compounds by the microorganisms. In the first complete analysis, made on May 24, about 10 gm. of organic matter was found to have been synthesized by the micro-

organisms (14.70 total organic matter — 4.61 gm. cellulose = 10.09 gm. synthesized organic matter<sup>2</sup>). This organic matter contained 757 mgm. of nitrogen (896 mgm. total nitrogen — 139 mgm. ammonia-nitrogen = 757 organic nitrogen), or about 7.6 per cent nitrogen in the humus produced by

TABLE 3

*Influence of cellulose upon the preservation of ammonia and protein nitrogen in a sand medium*  
Per 1,000 gm. of sand medium

DATE OF ADDITION OR ANALYSIS	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	CASEIN	CELLU- LOSE	ORGANIC MATTER LEFT		pH	NITROGEN FOUND			NITROGEN LOST, PER CENT OF TOTAL ADDED
				Total (C x 1.724)	Cellu- lose		NH <sub>3</sub> -N	NO <sub>3</sub> -N	Total	
	mgm. N	mgm. N	gm.	gm.	gm.		mgm.	mgm.	mgm.	
Control† 2/11/35	954	.....	...	0.58	0	6.6	372	186	558	41.5
3/ 7	318	.....	10	.....	.....	...	...	...	.....	....
3/26	318*	.....	10*	.....	2.58	...	111	...	.....	....†
4/17	318*	.....	30*	.....	5.97	...	224	...	.....	....†
5/24	.....	.....	...	14.70	4.61	7.0	139	0	896	6.1
6/14-8/18	636	.....	100	.....	.....	...	...	...	.....	....
9/18	.....	.....	25	30.19	15.97	5.4	156	1.2	1,426	10.3
2/11/35	1,590§	.....	175§	18.90	7.15	6.2	137	1.7	1,265	20.4
Control† 2/11/35	.....	2,448	...	1.38	0	6.7	16	118	298	88.0
3/ 7	.....	408	10	.....	.....	...	...	...	.....	....
3/26	.....	408*	10*	.....	6.21	...	94	...	.....	....†
4/17	.....	816*	30*	.....	5.81	...	85	...	.....	....†
5/24	.....	.....	...	10.43	1.34	7.5	17	...	928	43.1
6/14-8/18	.....	1,632	100	.....	.....	...	...	...	.....	....
9/18	.....	.....	25	12.59	Trace	6.3	18	92	1,422	56.4
2/11/35	.....	3,264§	175§	10.62	0.41	7.1	10	76	1,182	63.8

\* Added after analysis was made.

† The data presented here for control pots report only the total amounts of nitrogen added and found; see table 1 for details.

‡ The loss of nitrogen cannot be calculated for these analyses since no total nitrogen determinations were made.

§ Total nitrogen or cellulose added per pot.

|| Added only on 11/10.

the microorganisms as a result of the decomposition of the cellulose. In the second complete analysis (9/18/34), 14.2 gm. of synthesized organic matter was found per pot; this organic matter contained 1,269 mgm. of nitrogen, or

<sup>2</sup> These figures would have to be modified on the basis of the difference in carbon content of residual cellulose and of humus, since the total was calculated by means of the arbitrary factor, 1.724.

8.8 per cent. The loss of the nitrogen in the pots receiving cellulose was very small, namely, 10.3 per cent, as compared with 43.6 per cent loss of nitrogen in the corresponding pots which did not receive any cellulose. In the third complete analysis (2/11/35), there was found per pot 11.75 gm. of synthesized

TABLE 4

*Influence of cellulose and lignin upon the preservation of ammonia and protein nitrogen in a sand medium*

Per 1,000 gm. of sand medium

DATE OF ADDITION OR ANALYSIS	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>  mgm. N	CASEIN  mgm. N	CELLU- LOSE  gm.	LIGNIN  gm.	ORGANIC MATTER LEFT		pH	NITROGEN FOUND			NITRO- GEN LOST, PER CENT OF TOTAL ADDED
					Total (C x 1.724)	Cellulose		NH <sub>3</sub> -N	NO <sub>2</sub> -N	Total	
					gm.	gm.		mgm.	mgm.	mgm.	
Control* 2/11/35	954	.....	...	..	0.58	0	6.6	372	186	558	41.5
3/ 7	318	.....	10	5	.....	.....	...	...	...	.....	..
3/26	.....	.....	...	..	.....	3.75	...	106	...	.....	..†
3/29	318	.....	10	5	.....	.....	...	...	...	.....	..
4/17	.....	.....	...	..	.....	4.61	...	243	...	.....	..†
4/19-5/ 4	318	.....	30	15	.....	.....	...	...	...	.....	..
5/24	.....	.....	...	..	30.03	7.63	6.2	246	0	1,056	+10.7
6/14-8/18	632	.....	100	..	.....	.....	...	...	...	.....	..
9/18	.....	.....	25‡	..	71.72	23.64	5.3	151	3	1,741	+9.5
2/11/35	1,590‡	.....	175‡	25‡	50.86	16.87	5.4	118	2	1,727	+8.6
Control* 2/11/35	.....	2,448	...	..	1.38	0	6.7	16	118	298	88.0
3/ 7	.....	408	10	5	.....	.....	...	...	...	.....	..
3/26	.....	.....	...	..	.....	4.20	...	115	...	.....	..†
3/29	.....	408	10	5	.....	.....	...	...	...	.....	..
4/17	.....	.....	...	..	.....	6.71	...	263	...	.....	..†
4/19-5/ 4	.....	816	30	15	.....	.....	...	...	...	.....	..
5/24	.....	.....	...	..	29.41	0.86	6.4	15	3	1,312	19.6
6/14-8/18	.....	1,632	100	..	.....	.....	...	...	...	.....	..
9/18	.....	.....	25‡	..	41.72	Trace	5.9	11	50	1,929	40.9
2/11/35	.....	3,264‡	175‡	25‡	38.29	1.94	6.1	10	18	1,690	48.2

\* See table 1.

† No total nitrogen determinations made.

‡ Total added.

§ Added on 11/10.

organic matter, containing 1,126 mgm. of nitrogen, or 9.6 per cent. With the advance of decomposition, the nitrogen content of the residual humus becomes greater, with the result that more and more of the nitrogen is lost. After 2 months, the loss was only 6 per cent of the nitrogen; this increased to 10 per cent after 6 months, and to 20 per cent after 11 months.

When casein was used as a source of nitrogen, similar results were obtained. However, because of the fact that a much larger amount of nitrogen has been added per pot, a greater comparative loss was found to have taken place. After 2.5 months of decomposition (5/24/35), 9.1 gm. of organic matter was synthesized. This organic matter contained 911 mgm. of nitrogen, or 10 per cent on the basis of the humus produced. The same thing is true of the

TABLE 5

*Influence of cereal straw upon the preservation of ammonia and protein nitrogen in a sand medium*  
Per 1,000 gm. of sand medium

DATE OF ADDITION OR ANALYSIS	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	CASEIN	STRAW	ORGANIC MATTER LEFT TOTAL (C x 1.724)	pH	NITROGEN FOUND			NITROGEN LOST, PER CENT OF TOTAL ADDED
						NH <sub>4</sub> -N	NO <sub>3</sub> -N	Total	
	mgm. N	mgm. N	gm.	gm.		mgm.	mgm.	mgm.	
Control* 2/11/35	954	.....	...	0.58	6.6	372	186	558	41.5
3/ 7	318	.....	25	.....	...	...	...	.....	....
3/26	318†	.....	25†	.....	...	30	...	.....	....‡
4/17	318†	.....	50†	.....	...	165	...	.....	....‡
5/24	.....	.....	...	45.99	5.2	60	69	1,703§	+25.6
6/14-7/27	636	.....	50	.....	...	...	...	.....	....
9/18	.....	.....	...	58.27	5.1	19	164	1,842	15.2
2/11/35	1,590**	.....	150**	47.55	5.5	9	102	1,475	32.9
Control* 2/11/35	.....	2,448	...	1.38	6.7	16	118	298	88.0
3/ 7	.....	408	25	.....	...	...	...	.....	....
3/26	.....	408†	25†	.....	...	180	...	.....	....‡
4/17	.....	816†	50†	.....	...	21	...	.....	....‡
5/24	.....	.....	...	27.93	7.9	19	23	1,506§	26.0
6/14-7/27	.....	816	50	.....	...	...	...	.....	....
9/18	.....	.....	...	35.34	7.4	12	32	1,750	42.7
2/11/35	.....	2,448**	150**	24.22	6.9	9	116	1,542	49.5

\* See table 1.

† Added after analysis was made.

‡ No total nitrogen determination made.

§ Accounting also for the 405 mgm. of nitrogen in 100 gm. of straw.

|| Accounting also for the 607 mgm. of nitrogen in 150 gm. of straw.

\*\* Total added.

second complete analysis, when for 12.6 gm. organic matter synthesized, the organisms transformed 1,312 mgm. of nitrogen into organic forms, equivalent to 10.4 per cent. After 11 months, the amount of organic matter synthesized was 10.2 gm.; this contained 1,096 mgm. nitrogen, or 10.7 per cent. Here, as well, with an increase in the decomposition period, there were a reduction in the amount of humus synthesized and an increased loss of nitrogen. Because

of the excess of nitrogen added in the form of casein, a greater loss of this element took place even in the presence of cellulose. However, the loss was reduced from 88 per cent in the control pots to 64 per cent in the cellulose cultures. Had a greater amount of cellulose or a smaller amount of casein been used, the losses would no doubt have been reduced much further. It is of interest to record here that in all the cellulose pots, nitrate formation was considerably delayed.

The addition of both cellulose and lignin to the pots brought about an added effect upon the preservation of the nitrogen in the sand medium (table 4). In the case of the ammonium salt, all the nitrogen was preserved; there was actually a small gain in the nitrogen content, which may possibly be due to

TABLE 6  
*Influence of different forms of nitrogen upon the decomposition of straw*

SOURCE OF NITROGEN	STRAW USED	NITROGEN ADDED	PERIOD OF DECOMPOSITION	TOTAL ORGANIC MATTER LEFT (C x 1.724)	HEMI-CELLULOSE LEFT	CELLULOSE LEFT	LIGNIN LEFT
	gm.	mgm.	days	gm.	gm.	gm.	gm.
Control*.....	50	202†	..	45.00	11.84	15.93	6.00
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> .....	50	632	41	.....	.....	11.16‡	.....
Casein.....	50	816	41	.....	.....	7.40‡	.....
Control*.....	100	404†	..	90.00	23.68	31.86	12.00
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> .....	100	954	78	45.99	8.37	12.82	16.44
Casein.....	100	1,632	78	27.93	4.78	8.42	12.04
Control*.....	150	606†	...	135.00	35.52	47.79	18.00
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> .....	150	1,590	195	58.27	6.50	8.86	25.18
Casein.....	150	2,448	195	35.34	1.94	1.08	16.76
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> .....	150	1,590	310	47.55	4.42	8.22	17.51
Casein.....	150	2,448	310	24.22	1.56	1.06	14.04

\* Original straw.

† Nitrogen in straw.

‡ Including hemicelluloses.

the activities of nitrogen-fixing bacteria. This gain was evident in all the analyses made. In the pots receiving casein, there was still a considerable loss of nitrogen; however, this loss was reduced after 6 months from 53.8 per cent for the cultures containing lignin alone, and from 56.4 per cent for those containing cellulose alone, to 40.9 per cent when both cellulose and lignin were added. After 11 months, the loss again increased, as a result of the decomposition of some of the synthesized humus. In these pots as well, there was a much greater decomposition of the cellulose, and less humus formed than with ammonium phosphate as a source of nitrogen.

The action of straw in preserving the two forms of nitrogen in the sand medium (table 5) was quite similar to the effect of a mixture of cellulose and lignin. Here as well, the loss of nitrogen added in the form of an ammonium

salt was almost completely stopped; a gain in nitrogen was actually found at the early stage of decomposition of the straw; with the advance in decomposition, however, a loss occurred, which gradually increased. In the case of the casein, the loss of the nitrogen was also reduced to an amount comparable to that lost in the presence of both cellulose and lignin. The presence of nitrogen in the form of protein favored much greater decomposition of the straw, especially the carbohydrates, as a result of which a smaller amount of organic matter accumulation took place.

It is of interest to analyze further the effect of the two forms of nitrogen upon the specific decomposition of the straw as a whole and of its constituent organic compounds in particular. For this purpose, some of the data reported in table 5 are condensed, and additional information is included for comparison (table 6). The results bring out emphatically the fact that casein as a source of nitrogen favors a much more rapid and more complete decomposition of the straw as a whole. The favorable effect of the casein is exerted not only upon the decomposition of the cellulose and hemicelluloses but also upon that of the lignin. This may be due to a number of factors: 1. There is less of the lignin-like complexes synthesized by the bacteria which develop and attack the carbohydrates in the presence of casein than by the fungi in the presence of the ammonium salt; 2. Some of the ligno-proteins formed in the presence of casein may decompose more rapidly than the lignin alone; 3. Protein may be a more favorable source of nitrogen for the lignin-decomposing organisms than is ammonium salt, as found in the case of the cultivated mushroom; 4. The less acid reaction of the sand cultures containing casein (pH 7.9) than of the ammonium phosphate cultures (pH 5.2) favored the development of actinomycetes and of other lignin-decomposing organisms; for example, *Coprinus*, a lignin-decomposing organism (3), was found to develop only in the lignin-cellulose-casein cultures.

#### SUMMARY

A study has been made of the influence of straw and of two of the most important groups of its constituents; namely, cellulose and lignin, in preventing the loss of nitrogen added to a sand medium in the form of an ammonium salt and a protein. The results obtained are sufficient to emphasize the fact that the preservation of the nitrogen in the soil depends on a number of factors, chief among which are the nature of the nitrogen source and the nature of the organic matter added to the soil. The loss of nitrogen from a sand medium was largely prevented, under the particular experimental conditions, by the use of certain forms of organic matter; this resulted in the preservation of the nitrogen in the soil in the form of humus. The rôles of the different plant constituents in the preservation of the nitrogen differ. The function of cellulose and of other carbohydrates consists in supplying energy for the activities of the microorganisms, with the result that the nitrogen is transformed into microbial cell substance; the function of lignin consists in its action as a buffer for the absorption of the ammonia and in the fixation of the protein.



## REFERENCES

- (1) COLLISON, R. C., AND CONN, H. J. 1925 The effect of straw on plant growth. N. Y. Agr. Exp. Sta. Bul. 114.
- (2) SCHEFFER, F., AND KARAPURKAR, Y. M. 1934 Die Abhängigkeit der Nitrifikation von der Zusammensetzung und der Abbauschwindigkeit der organischen Substanz. *Kühn Arch.* 37: 143-172.
- (3) WAKSMAN, S. A. 1931 Decomposition of the various chemical constituents, etc. of complex plant materials by pure cultures of fungi and bacteria. *Arch. Mikrobiol.* 2: 136-154.
- (4) WAKSMAN, S. A., AND HEUKELEKIAN, H. 1924 Cellulose decomposition by various groups of soil microorganisms. *Actes IV Conf. Internat. Pedol.* 3: 216-327.
- (5) WAKSMAN, S. A., AND HUTCHINGS, I. J. 1935 The function of cellulose and lignin in the preservation of nitrogen in soils and in composts. *Proc. Third Internat. Soil Sci. Cong.* 1: 163-167.
- (6) WAKSMAN, S. A., AND IYER, K. R. N. 1932 Contribution to our knowledge of the chemical nature and origin of humus: I. On the synthesis of the "humus nucleus"; II. The influence of "synthesized" humus compounds and of "natural humus" upon soil processes. *Soil Sci.* 34: 43-79.



## AUTHOR INDEX

- Allen, M. C. *See* Vandecaveye, S. C.
- Allison, L. E. Organic soil carbon by reduction of chromic acid, 311-320.
- Allison, R. V. Jacob G. Lipman as teacher and director of research, 31-36; *see* Neller, J. R.
- Andrews, W. B. Effect of nitrogen content of rye on its rate of decomposition, 219-221.
- Bartholomew, R. P. Fluorine, its effect on plant growth and its relation to the availability to plants of phosphorus in phosphate rocks, 203-217.
- Baver, L. D., and Winterkorn, H. Sorption of liquids by soil colloids: II. Surface behavior in the hydration of clays, 403-419.
- Blair, A. W. Jacob G. Lipman and New Jersey agriculture, 25-29.
- Bollen, W. B. *See* Powers, W. L.
- Bouyoucos, G. J. Comparison between the suction method and the centrifuge method for determining the moisture equivalent of soils, 165-171; method for making mechanical analysis of the ultimate natural structure of soil, 481-485.
- Brown, P. E. Beginnings and development of soil microbiology in the United States, 49-58.
- Carter, L. S. Some chemical and biological changes produced in a Fox sandy loam by certain soil management practices, 223-236.
- Cole, R. C., and Edlefsen, N. E. Sedimentation tube for analyzing water-stable soil aggregates, 473-479.
- Davis, L. E. Sorption of phosphates by non-calcareous Hawaiian soils, 129-158.
- Denison, I. A., and Ewing, S. P. Corrosiveness of certain Ohio soils, 287-299.
- Doughty, J. L. Phosphate fixation in soils, particularly as influenced by organic matter, 191-202.
- Eaton, F. M., and Sokoloff, V. P. Absorbed sodium in soils as affected by the soil-water ratio, 237-247.
- Edlefsen, N. E. *See* Cole, R. C.
- Ewing, S. P. *See* Denison, I. A.
- Fudge, J. F. Mathematical relationships between total exchange capacity and absorption of ammonium and potassium by soils, 269-284.
- Harris, H. C. Comparison of potassium permanganate and ceric sulfate for the oxidation of cobaltinitrite in the estimation of potassium in KCl solution and in ammonium acetate soil-extracts, 301-309.
- Hutchings, I. J. *See* Waksman, S. A.
- Jenny, H. Clay content of the soil as related to climatic factors, particularly temperature, 111-128.
- Joffe, J. S., Kardos, L. T., and Mattson, S. Laws of soil colloidal behavior: XVII. Magnesium silicate—its base-exchange properties, 255-268.
- Kardos, L. T. *See* Joffe, J. S., and Mattson, S.
- Kelley, W. P. Agronomic importance of calcium, 103-109.
- Lamb, John Jr. Availability of soil potassium, 365-381.
- Lundegårdh, H. Influence of the soil upon the growth of the plant, 89-101.
- Lutz, J. F. Relation of soil erosion to certain inherent soil properties, 439-457.
- Mail, G. A. Soil temperature apparatus for field work, 285-286.
- Mann, H. B. Relation of soil treatment to the nodulation of peanuts, 423-437.
- Mattson, S. *See* Joffe, J. S., Kardos, L. T., and.
- Musgrave, G. W. Device for measuring precipitation waters lost from the soil as surface runoff, percolation, evaporation, and transpiration, 391-401.
- Neller, J. R., and Allison, R. V. Machine for the subsurface treatment of soils with chloropicrin and with carbon bisulfide for nematode control under field conditions, 173-179.
- Powers, W. L., and Bollen, W. B. Chemical and biological nature of certain forest soils, 321-329.

- Puri, A. N.** New method of estimating exchangeable bases in soils, 159-163; estimation of replaceable Na and K, exchange capacity, and degree of alkalization in alkali soils by ammonium carbonate extraction, 249-253; simple method of estimating exchangeable calcium and other bases in non-calcareous soils, 383-390.
- Ratner, E.** Influence of exchange sodium in the soil on its properties as a medium for plant growth, 459-471.
- Russell, E. J.** Jacob G. Lipman and soil science, 3-7.
- Schreiner, O.** Early fertilizer work in the United States, 39-47.
- de'Sigmond, A. A. J.** Development of soil science, 77-86.
- Snow, L. M.** Comparative study of the bacterial flora of wind-blown soil: VI. Death Valley, California, with summary of six soil studies, 181-190.
- Sokoloff, V. P.** See **Eaton, F. M.**
- Vandecaveye, S. C.,** and Allen, M. C. Microbial activities in soil: II. Activity of specific groups of microbes in relation to organic matter transformation in Palouse silt loam, 331-343.
- Waksman, S. A.** Jacob G. Lipman as an investigator, 11-23.
- Waksman, S. A.,** and Hutchings, I. J. Chemical nature of organic matter in different soil types, 347-363; rôle of plant constituents in the preservation of nitrogen in the soil, 487-497.
- Winogradsky, S.** Method in soil microbiology as illustrated by studies on Azotobacter and the nitrifying organisms, 59-76.
- Winterkorn, H.** See **Baver, L. D.**

## SUBJECT INDEX

- Absorption—
  - equations—
    - Csiky, 279
    - Patten and Waggaman, 280
    - Wiegner, 282
  - of ammonia and potassium by soils and its relation to exchange capacity, 269
- Alfalfa, nitrate production from additions of, 229.
- Ammonium—
  - absorption of, by soils, 269.
  - acetate soil extract, composition of, 240.
  - complex, hydrolysis of, 277.
  - salts, rate of nitrification, 227.
  - sulfate, influence on capillary movement of water, 463.
- Anions, extraction of, from soils with water, ammonium-acetate, and by displacement, 240.
- Azotobacter—
  - method in soil microbiology as illustrated by studies on, 59.
  - soil conditions affecting activity of, 62.
- Bacteria—
  - flora in soils of Death Valley, California, 181.
  - in wind-blown soil, 181.
  - nitrifying, the method in soil microbiology as illustrated by studies on, 59.
  - numbers of, in relation to soil treatment, 227.
- Base-exchange—*see also* Exchange capacity, Cations.
- capacity—
  - estimation by ammonium carbonate extraction, 249.
  - relation to calcium, 107.
- complex—
  - ammonia substitution in the, and phosphorus absorption, 143.
  - potassium substitution in the, and phosphorus absorption, 143.
- properties of magnesium-silicate, 255.
- Bases—
  - concentration of, in aqueous and absorbed phases, 245.
- exchangeable—
  - ammonium carbonate method of determining, 249.
  - barium hydroxide method of determining, versus other, 250.
  - errors involved in determining, 243.
  - extraction with water, ammonium acetate, and by displacement, 240.
  - method of estimating, 159, 383.
  - presence of, in filtrates after fixation of phosphate by soil, 144.
- Bentonite—
  - swelling and viscosity of, 448.
  - water intake by, 405.
- Boron, importance in plant growth, 99.
- Calcium—*see also* Lime.
  - agronomic importance of, 103-109.
  - cyanamid, influence on capillary movement of water, 463.
- exchangeable—
  - as affected by cropping, 373.
  - method of estimating, in non-calcareous soils, 383-390.
  - relationship between, and magnesium-silicate complex, 263.
  - relation to exchangeable potassium, 372.
- relation between, in the soil and its concentration in plants, 97.
- relation to—
  - alkali soils, 106.
  - base-exchange capacity, 107.
  - fertilizer, 108
  - phosphate availability, 104.
  - plant growth, 104.
  - soil formation, 105.
  - soil structure, 105.
- sulfate, effect on nodulation of peanuts, 425.
- Carbon—
  - dioxide production—
    - and organic carbon and nitrogen balance, 337.
  - as affected by plant residues, 235.
  - from cellulose, 230.
  - relation to nitrification, bacterial numbers, etc., 232.

- Carbon—(*continued*)  
organic soil, by reduction of chromic acid 311.
- Carrol, John Sharkey, an obituary note, 421.
- Cations, effect on—  
permeability of clay membranes, 451.  
viscosity and swelling of clays, 448.
- Cellulose—  
carbon-dioxide production from, 230.  
influence of, on nitrogen preservation in a sand medium, 492.
- Ceric sulfate versus potassium permanganate for the oxidation of cobaltinitrite, 301.
- Chernozem—  
composition of humus in, 358.  
filterability of, as influenced by exchangeable sodium, 463.
- Chestnut soils, composition of humus in, 359.
- Clay—  
content of soil as related to climatic conditions, 111-128.  
hydration of colloidal, 447.  
moisture function, 120.  
surface behavior in the hydration of, 403.
- Colloidal—  
behavior, the laws of soil, 255.  
clay membranes, permeability of, 450.
- Colloids—  
chemical composition of, of Iredell, Davidson, and Putnam, 445.  
physico-chemical properties of, 409.  
properties of, affecting erosion, 444.  
sorption of liquids by soil, 403-419.  
swelling of soil, 412, 449.
- Copper, importance in plant growth, 99.
- Cotton seed meal, nitrate production from, 229.
- Cowpeas, phosphorus and fluorine content of, grown in solution cultures, 207.
- Dispersion and erosion ratios, 444.
- Earthworms in forest soils, 324.
- Exchange—  
capacity, mathematical relations between total, and absorption of ammonia and potassium by soils, 269-284.  
properties, effect on hydration of colloidal clays, 415.
- Fertilizer—  
effects with and without lime, 233.  
work in the United States, 39-47.
- Fertilizers, relation of, to calcium, 108.
- Fluorine—  
bearing phosphates, availability of, 208.  
effect of, on plant growth and its relation to availability of phosphorus in rock phosphate, 203-217.
- Fungi, numbers of, in relation to soil treatment, 227.
- Humus, phosphate fixation by, 195.
- Hydrogen—  
ion concentration, effect on—  
phosphate fixation, 147.  
plant growth, 95.  
potassium fixation, 148.  
peroxide, fixation of phosphorus by peat treated with, 197.
- Lignin, influence on nitrogen preservation in sand medium, 490.
- Lime, effect on—  
crop yield, 234.  
nodulation of peanuts, 425.
- Lipman, J. G.—  
biographical sketch, 1-2.  
investigator, 11-23.  
New Jersey agriculture and, 25-29.  
teacher and director of research, 31-36.
- Lysimeters, type of, for study of runoff and percolation, 391.
- Magnesium—  
relation between calcium and, in the soil and its concentration in plants, 97.  
silicate, its base-exchange properties, 255.
- Manganese—  
importance of, in plant growth, 99.  
intake by plants in relation to calcium content of soil, 98.
- Marbut, Curtis F., an obituary note, 345.
- Microbiology—*see also* Bacteria.  
development of soil, in the United States, 49-58.  
method in soil, 59-76.
- Microorganisms—  
activity of, in soil, 331-343.  
in forest soil profiles, 323.  
specific groups of, effect on organic matter transformation, 338.  
straw affecting activity of, 336.
- Moisture—  
equivalent of soils, determination of, 165-171.  
influence on clay content of soils, 120.  
loss as surface runoff, percolation, evaporation, and transpiration, 391.

- Nematodes, control of, in soils with sub-surface treatment, 173.
- Nitrate production from various materials, 229.
- Nitrification—  
rate of, of urea and ammonium salts, 227.  
relation to carbon dioxide production, bacterial numbers, and crop yield, 232.  
soil processes and their relation to, 228.
- Nitrogen—  
availability in forest soil layers, 325.  
balance, relation to carbon dioxide production, 337.  
content of rye and its effect on decomposition, 219.  
effect on capillary movement of water in soils, 463.  
fixation in Death Valley soils, 188.  
lignin effect on preservation of, 490.  
preservation in the soil, 487.
- Oats, influence of exchangeable sodium on, 460.
- Organic matter—  
chemical nature of, in different soil types, 347-363.  
chromic acid method of determining carbon in, 311.  
decomposition in soil, 340.  
phosphate fixation as affected by, 191.  
proximate composition of, at various periods, 341.  
Schollenberger method of determining carbon in, 318.  
transformation of, relation to activity of specific microbes, 331.
- Peanuts, relation of soil treatment to the nodulation of, 423.
- Peat—  
heat effects on fixation of phosphorus by, 198.  
phosphorus fixation as influenced by, 193.
- Phosphate—  
availability of, as related to calcium, 104.  
fixation of—  
by Hawaiian soils, 129.  
influenced by hydrogen-ion concentration, 147.  
influenced by organic matter, 191-202.  
in soils from which replaceable bases have been substituted, 143.  
ions, fixation of basic ions accompanying, 144.  
rock, *see* Rock phosphate.
- Phosphorus—  
availability of, from rock phosphate, 203.  
fluorine effect on availability of, to plants, 212.  
solubility of, in combination with various cations, 199.
- Plant—  
boron in, growth, 99.  
copper in, growth, 99.  
growth—  
anion effect on cation intake, 94.  
as influenced by the soil, 89.  
cation effect on anion absorption, 100.  
effect of fluorine on, 203.  
relation to calcium, 104.  
manganese in, growth, 99.  
nutrients—  
balance in medium, 93.  
relation of, in vegetation to nutrients in soil, 97.  
roots—  
fluorine absorption by, 207.  
mechanism of absorption of soil solution by, 94.
- Plants—  
fluorine and phosphorus content of, 206.  
phosphorus availability to, from rock phosphate, 203.
- Podzols, chemical composition of humus in, 353.
- Potassium—  
absorption of, by soils, 269.  
availability of soil, 365-381.  
cobaltinitrite method for estimating, 301, 366.  
exchangeable, as affected by—  
cropping, 373.  
fertilization, 373.  
permanganate versus ceric sulfate for the oxidation of cobaltinitrite, 301.  
relation—  
between inner concentration of, in leaves of oats and growth, 93.  
of exchangeable, to exchangeable calcium, 372.  
of total to exchangeable, 372.  
to available, in soil and its concentration in plants, 96.  
replaceable, estimation of, by ammonium carbonate extraction, 249.  
solubility rate of soil, 375.

- Rainfall, losses of water from, as surface runoff, percolation, evaporation, and transpiration, 391.
- Rock phosphate—  
phosphorus availability from, as affected by fluorine, 203.  
versus monocalcium phosphate, 211.
- Roots, fluorine presence in, 208; *see also* Plant roots.
- Rye, effect of nitrogen content of, on its rate of decomposition, 219–221.
- Serozem, composition of humus in, 359.
- Silica-sesquioxide ratio, effect on hydration of colloidal clays, 415.
- Sodium—  
absorbed, as affected by the soil-water ratio, 237–247.  
exchangeable, effect on—  
plant growth, 459–471.  
soil properties, 462.  
replaceable, estimation of, by ammonium-carbonate extraction, 249.
- Soil—  
acidity—  
estimation of total, 289.  
influence of, on corrosiveness of soil types, 293.  
relation to calcium, 103.  
aggregates, a sedimentation tube for analyzing water-stable, 473–479.  
bacterial flora in wind-blown, 181.  
clay content of the, as related to temperature, 111–128.  
colloidal behavior, laws of, 255–268.  
colloids, effect on ion absorption by plants, 94; *see also* Colloids.  
conditions affecting activity of *Azotobacter*, 62.  
Davidson series, mechanical and aggregate analysis of, 440.  
effect on plant growth, 89–101.  
erosion—  
effect on clay content of the, 117.  
relation to some inherent soil properties, 439–457.  
exchangeable sodium in the, its effects on plant growth, 459.  
extract—  
ammonium-acetate, 303.  
composition of 1:5, 238.  
formation, relation to calcium, 105.  
Iredell series, mechanical and aggregate analysis of, 440.  
loss of precipitation waters from the, 391–401.  
management practices affecting chemical and biological changes, 223–236.  
organic, carbon determination, 311.  
peanuts, nodulation as affected by, treatment, 423–437.  
potassium, *see* Potassium.  
preservation of nitrogen in the, as affected by plant constituents, 487–497.  
processes, relation to nitrification, 228.  
profile—  
corrosiveness of soil types and the degree of development of the, 297.  
microorganisms in, 323.  
science—  
and Jacob G. Lipman, 3–9.  
development of, 77–87.  
sedimentation tube for analyzing water-stable soil aggregates, 473.  
solution—  
displaced, salt content of, 238.  
mechanism of absorption of, by plant roots, 94.  
structure—  
and aggregates, 473.  
relation to calcium, 105.  
ultimate, natural method of determining, 481.  
temperature apparatus for field work, 285–286.  
types—  
organic matter in different, 347.  
properties and corrosiveness of, 289.  
water ratio, sodium absorption as influenced by, 237.  
wind-blown, bacterial flora in, 181–190.
- Soils—  
absorption of ammonia and potassium by, in relation to exchange capacity, 269.  
alkali—  
degree of alkalization of, method of estimating, 249.  
relation to calcium, 106.  
corrosiveness of certain Ohio, 287.  
Death Valley, California, character of, 181.  
exchangeable bases in, method of determining, 159–163.  
forest—  
chemical and biological nature of, 321–329.  
earthworms in, 324.  
nitrogen availability in, 325.



Soils—(*continued*)

Hawaiian, sorption of phosphates by, 129-158.

leaching, with acid and its effect on phosphate fixation, 192.

mechanical analysis of the ultimate natural structure of, 481-485.

moisture equivalent, *see* Moisture equivalent.

nematodes in, *see* Nematodes.

nitrification of nitrogenous materials in, 228.

Ohio, corrosiveness of certain, 287.

Oregon (Western), chemical characteristics of, 321.

Pennsylvania, chemical characteristics of, 321.

phosphate fixation in, 129, 191.

subsurface treatment of, for nematode control, 173-179.

Solonetz, characteristics of, 461.

Straw—

decomposition of, as affected by forms of nitrogen, 495.

effect on—

microbial activity, 336.

preservation of nitrogen in sand media, 494.

Sudan grass, growth of in presence of fluorine, 213.

Sulfur, effect on nodulation of peanuts, 425.

Urea—

influence on capillary movement of water, 463.

nitrification of, 227.

Wheat, influence of exchangeable sodium on, 460.

